Mechanistic insights on the controlled switch from oligomerization to polymerization of 1-hexene catalyzed by an NHC-zirconium complex

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Contents:

GC trace of the oligomers obtained:

All these experiments were realized with 1 000 equiv. of 1-hexene.

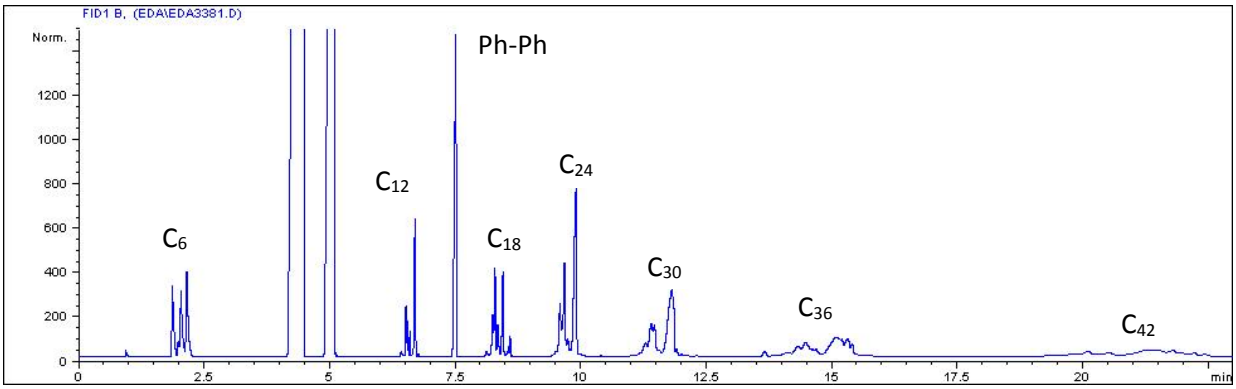


Figure S1. GC analysis of oligo(1-hexene)s obtained using **1**/[Ph_3C][$B(C_6F_5)_4$].

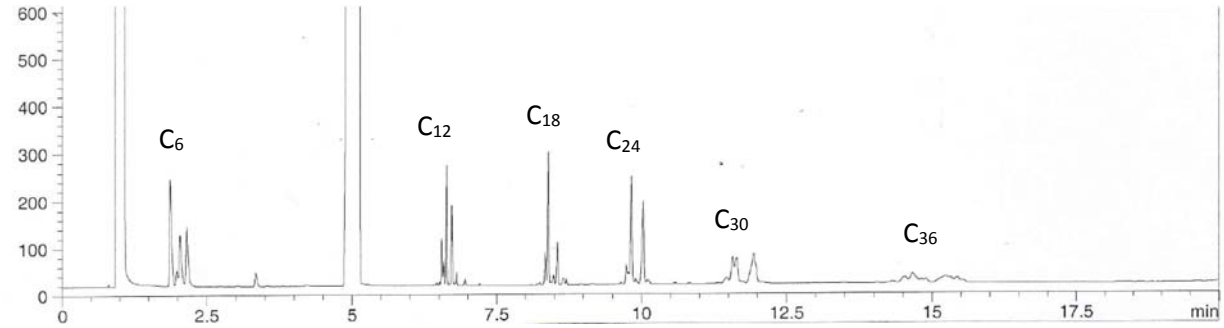


Figure S2: GC analysis of oligo(1-hexene)s obtained using **1**/1000 equiv. MAO.

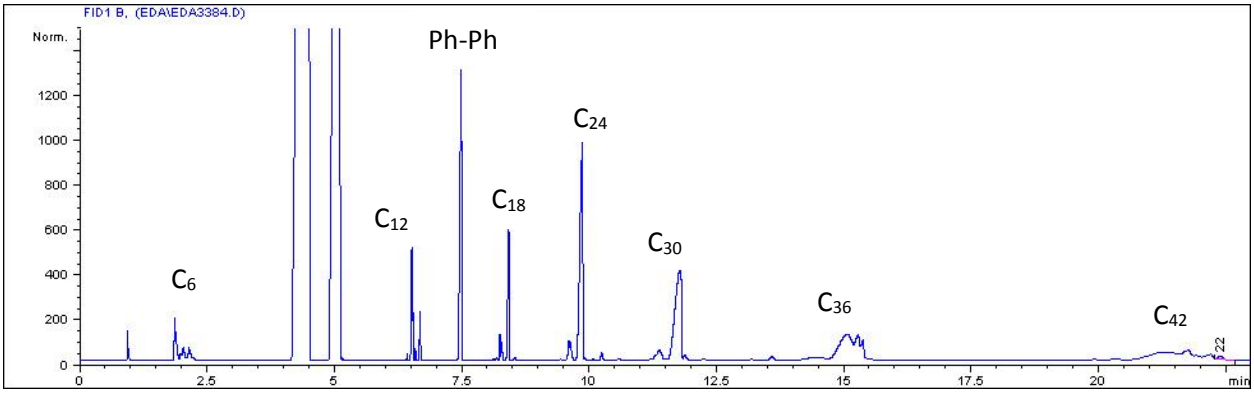


Figure S3. GC analysis of oligo(1-hexene)s obtained using **1**/[Ph_3C][$B(C_6F_5)_4$]/PPh_3.

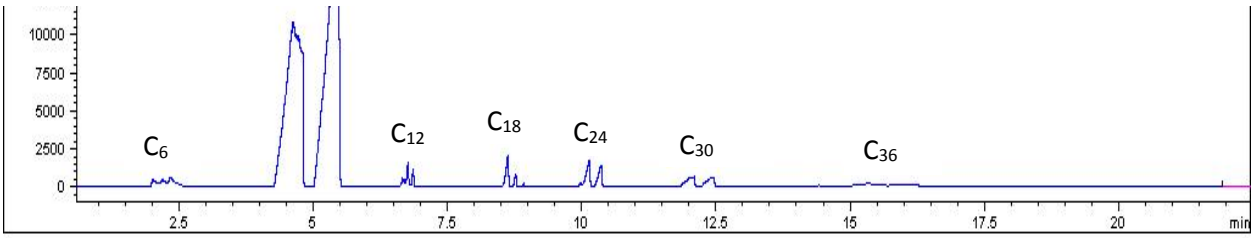


Figure S4. GC analysis of oligo(1-hexene)s obtained using **1**/[Ph_3C][$B(C_6F_5)_4$]/$PMes_3$.

NMR data:

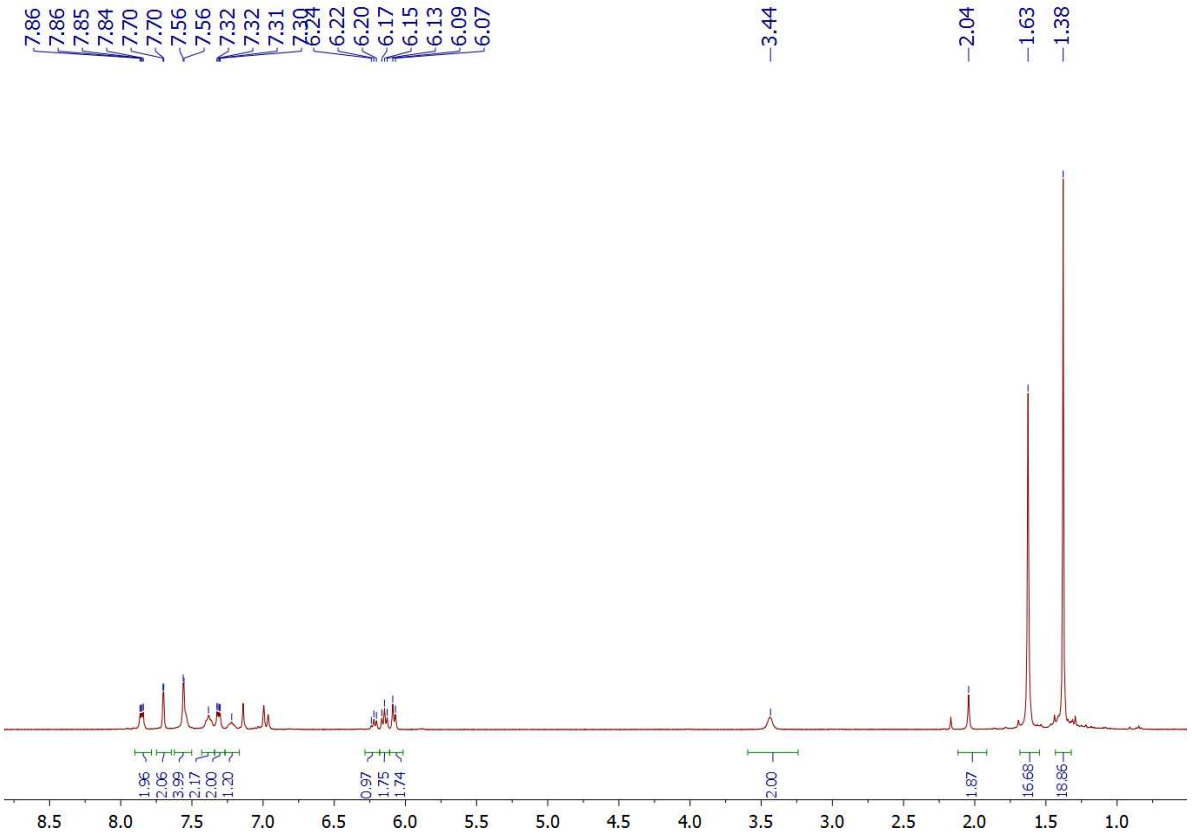


Figure S5: ^{1}H NMR (C_6D_5Cl, 25 ºC) of the reaction of complex **1** with $B(C_6F_5)$.

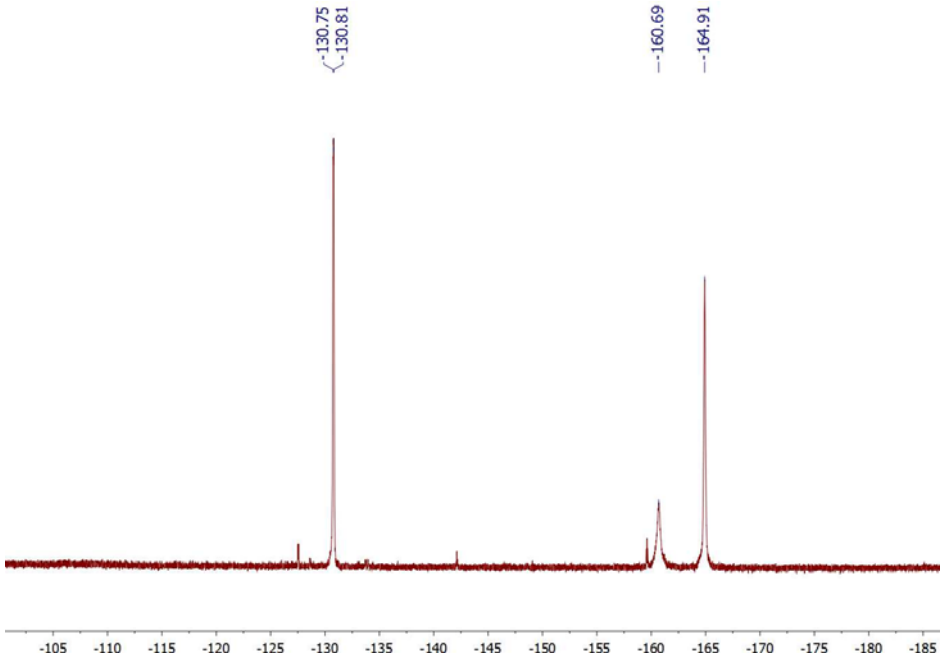


Figure S6: ^{19}F NMR (C_6D_5Cl, 25 ºC) of the reaction of complex **1** with $B(C_6F_5)$.

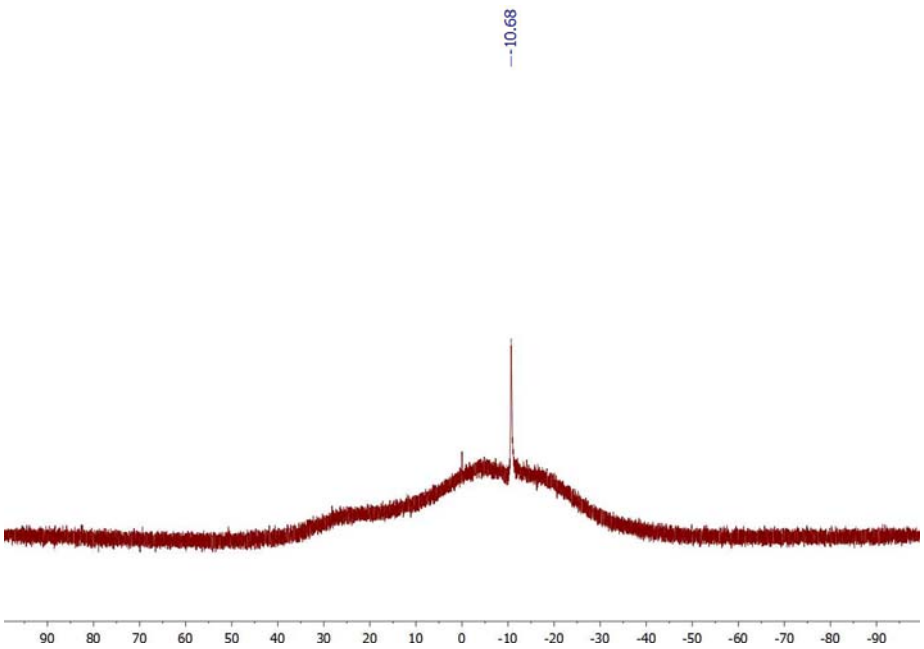


Figure S7: ^{11}B NMR (C_6D_5Cl, 25 ºC) of the reaction of complex **1** with $B(C_6F_5)$.

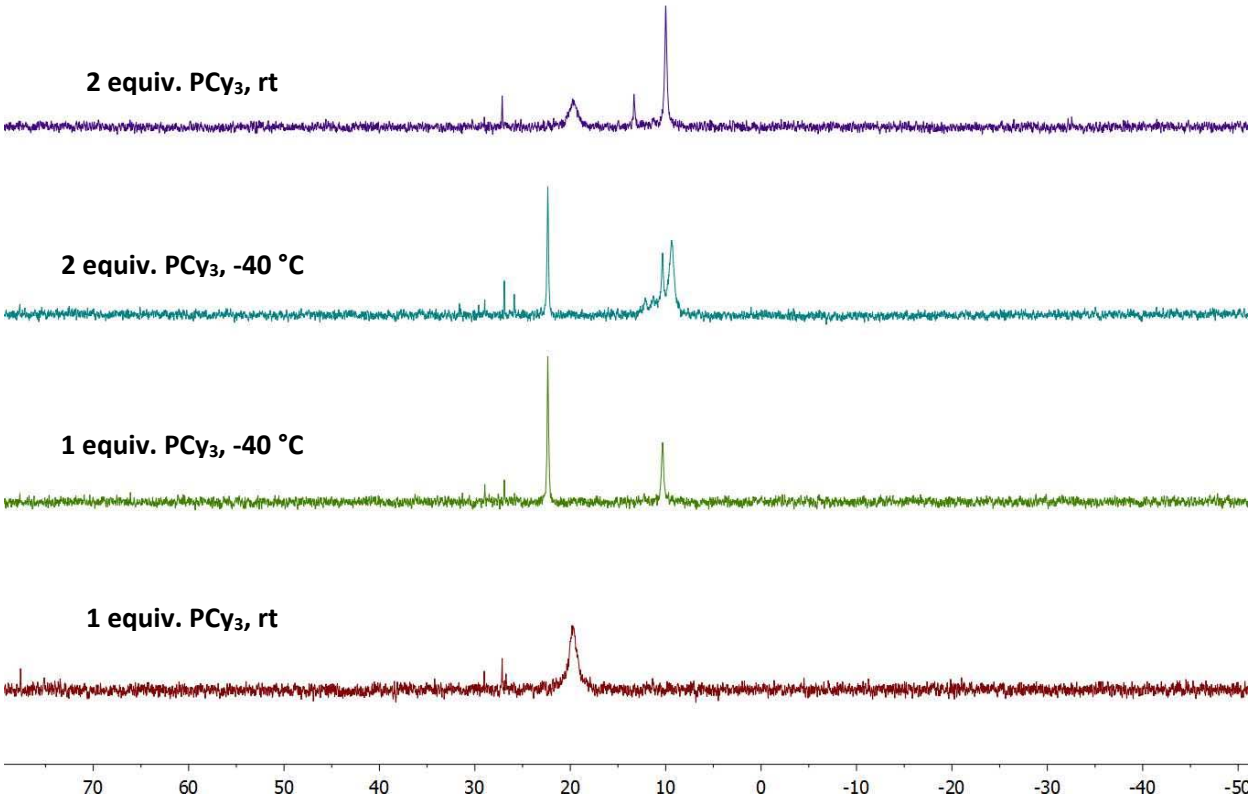


Figure S8: ^{31}P NMR (C_6D_5Cl) of the system **1**/$[Ph_3C][B(C_6F_5)_4]$/PCy_3 at different temperatures, with 1 or 2 equiv. of PCy_3.

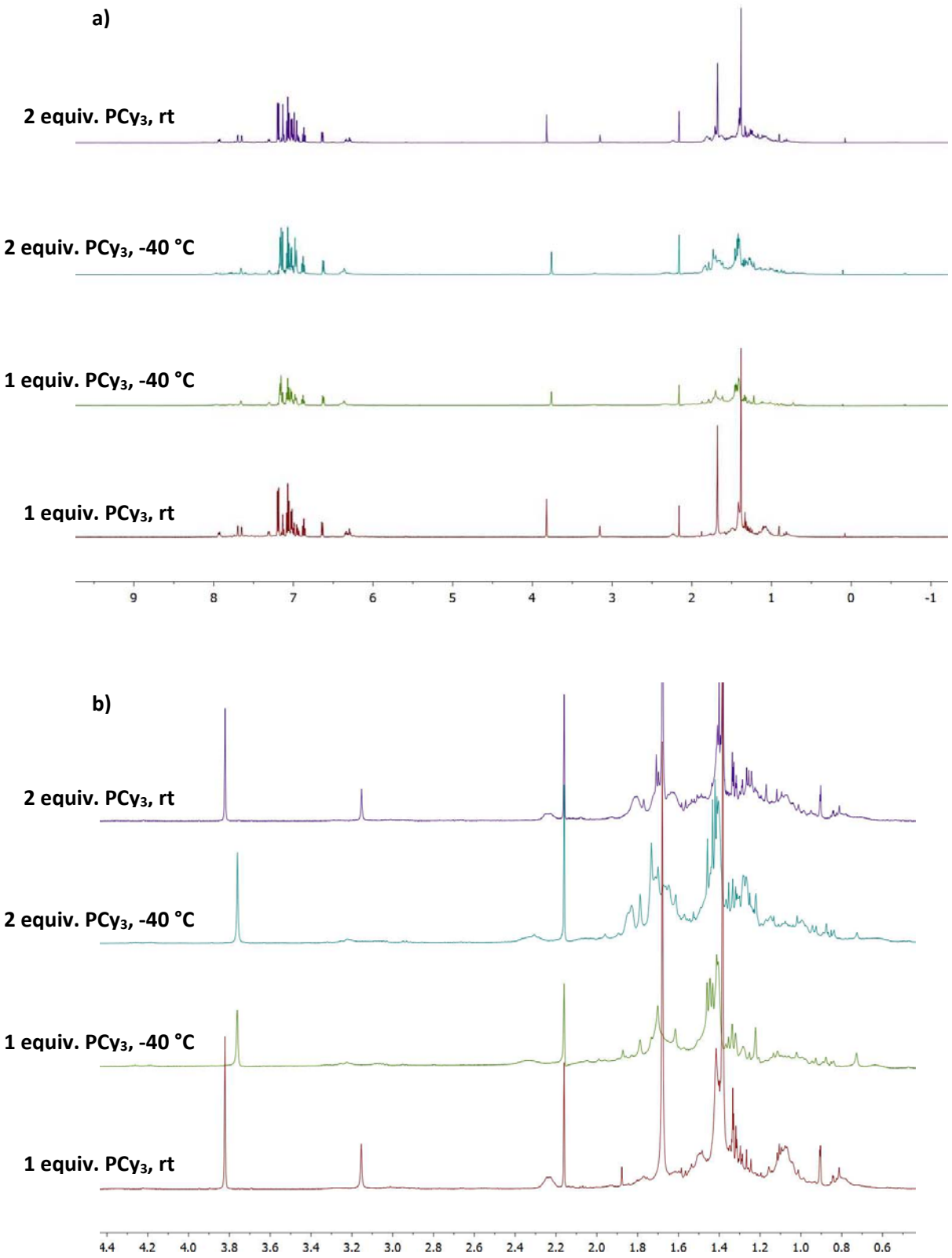


Figure S9: ^{1}H NMR (C_6D_5Cl) of the system **1**/$[Ph_3C][B(C_6F_5)_4]$/PCy_3 at different temperatures, with 1 or 2 equiv. of PCy_3: a) full spectrum, b) zoomed in the aliphatic region.

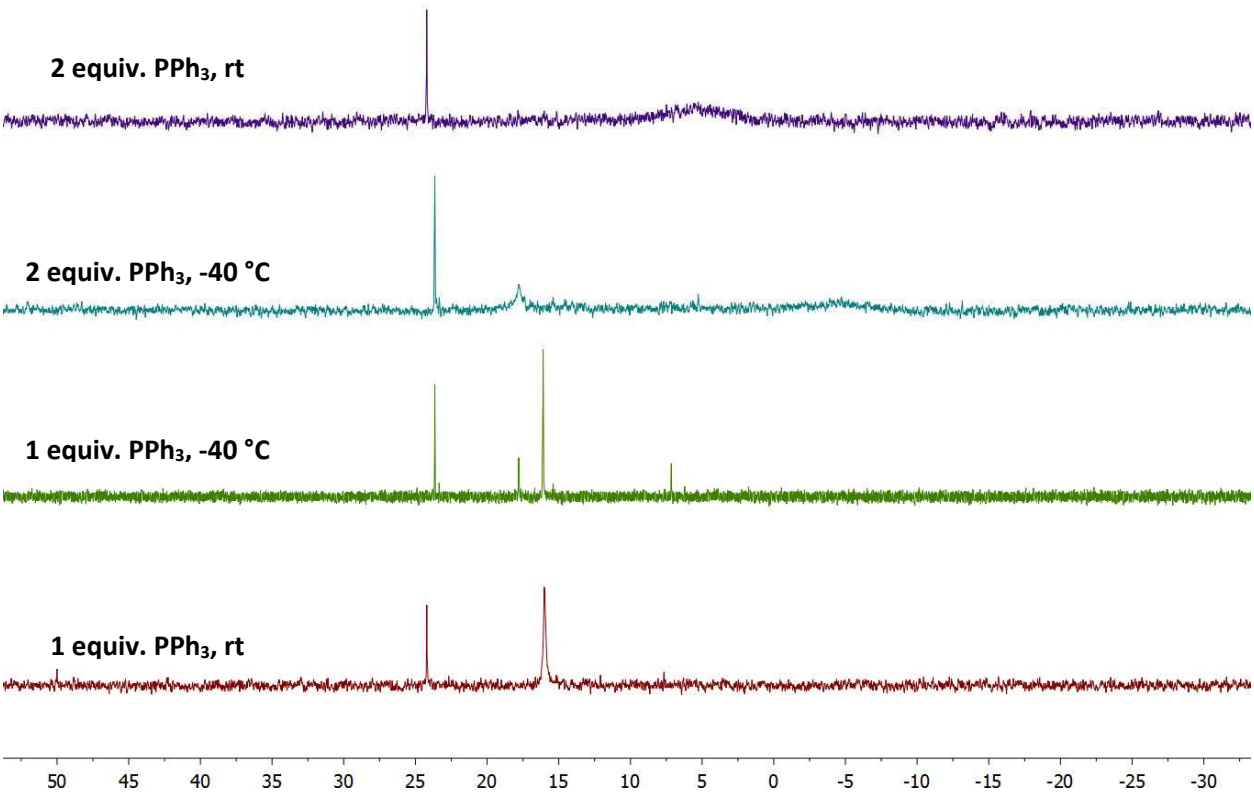


Figure S10: ^{31}P NMR (C_6D_5Cl) of the system **1**/[Ph_3C][$B(C_6F_5)_4$]/PPh_3 at different temperatures, with 1 or 2 equiv. of PPh_3.

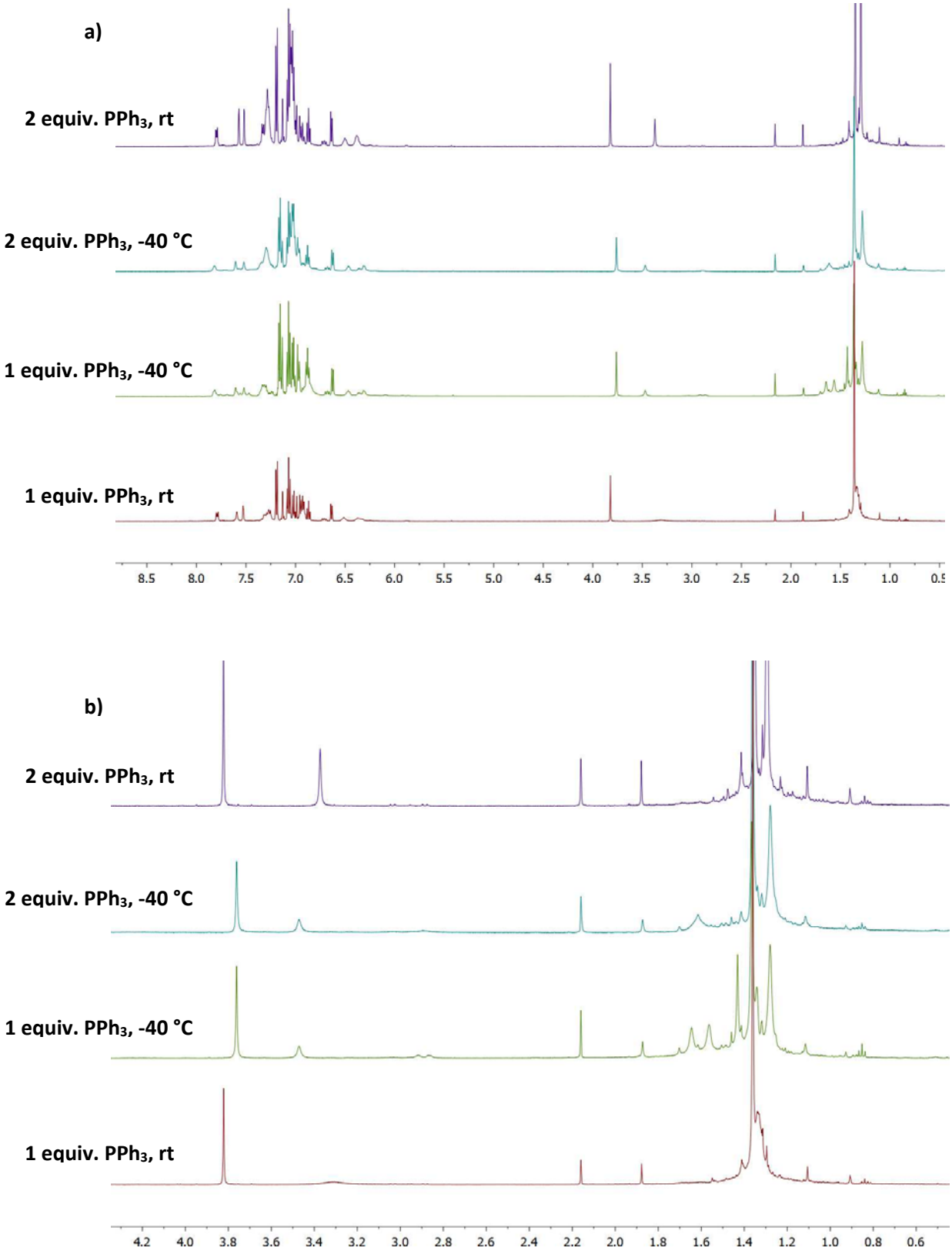


Figure S11: ^{1}H NMR (C_6D_5Cl) of the system **1**/$[Ph_3C][B(C_6F_5)_4]$/PPh_3 at different temperatures, with 1 or 2 equiv. of PPh_3: a) full spectrum, b) zoomed in the aliphatic region.

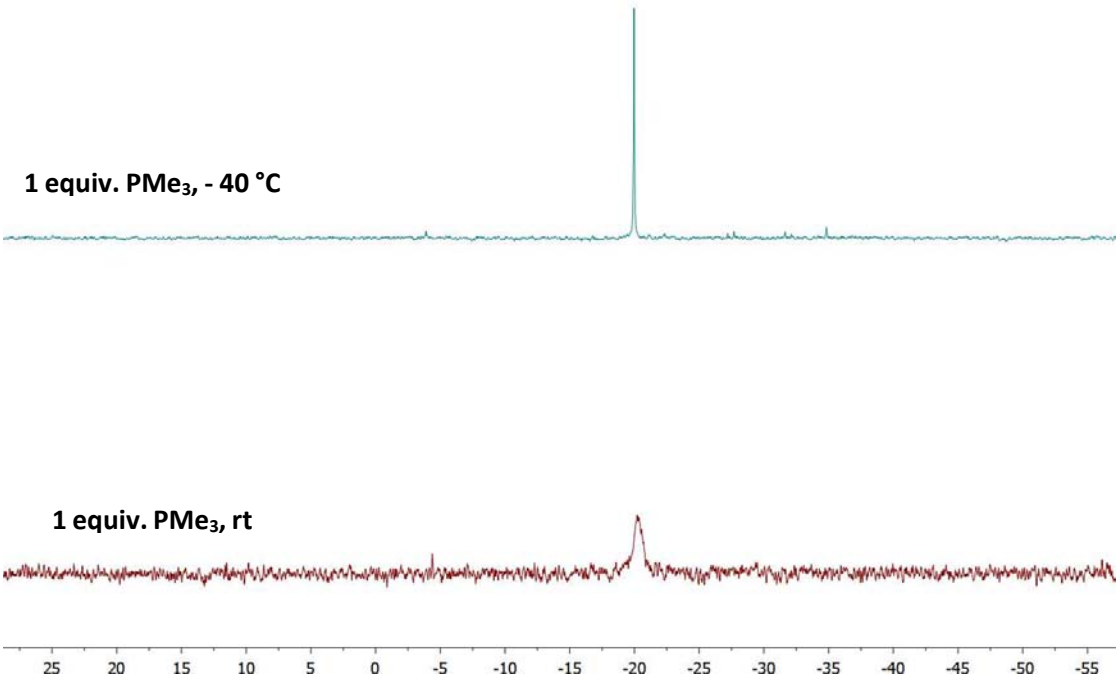


Figure S12: ^{31}P NMR (C_6D_5Cl) of the system **1**/[Ph_3C][$B(C_6F_5)_4$]/PMe_3 at different temperatures, with 1 equiv. of PMe_3.

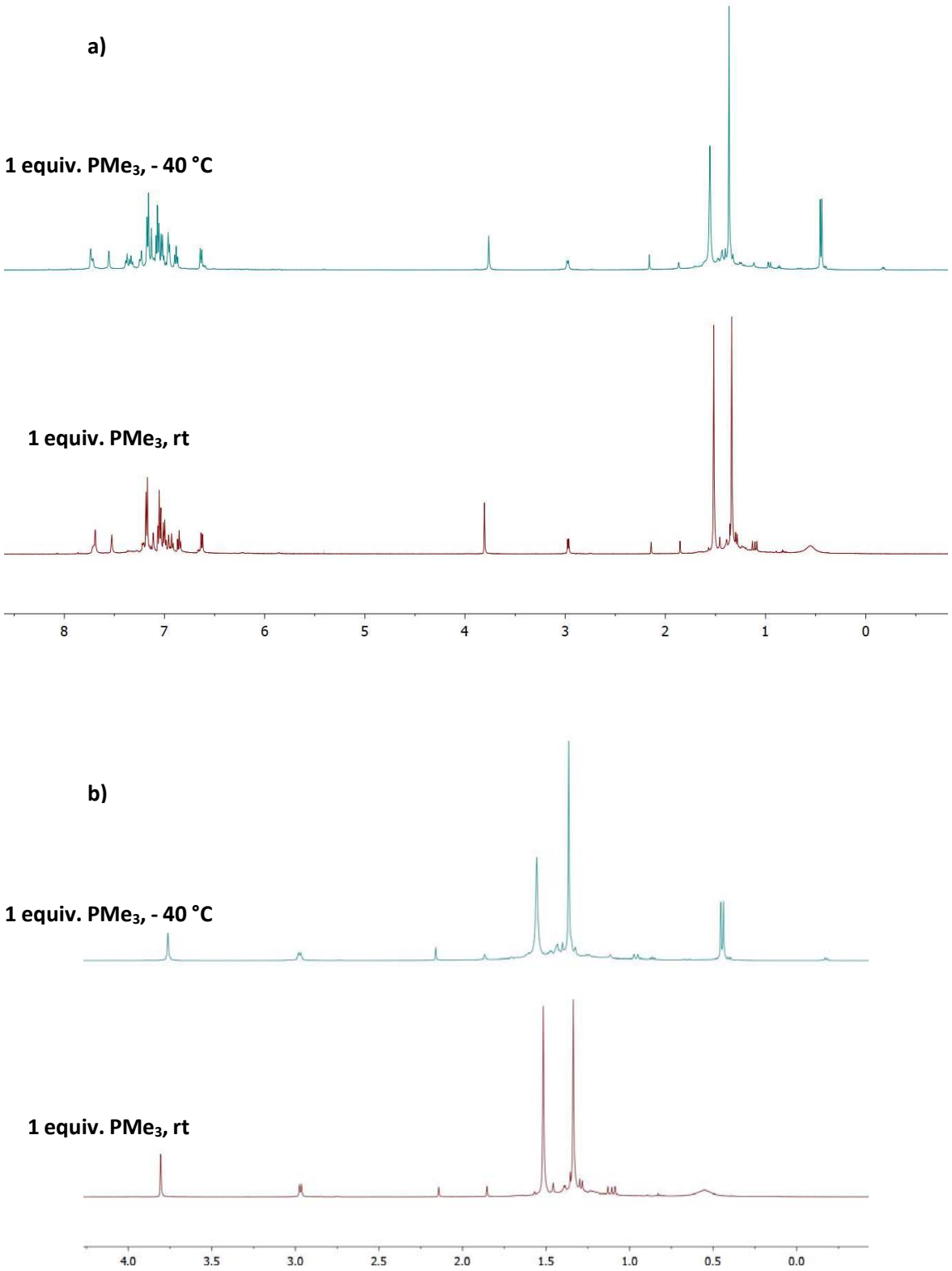


Figure S13: ^{1}H NMR (C_6D_5Cl) of the system **1**/$[Ph_3C][B(C_6F_5)_4]$/PMe_3 at different temperatures, with 1 equiv. of PMe_3: a) full spectrum, b) zoomed in the aliphatic region.

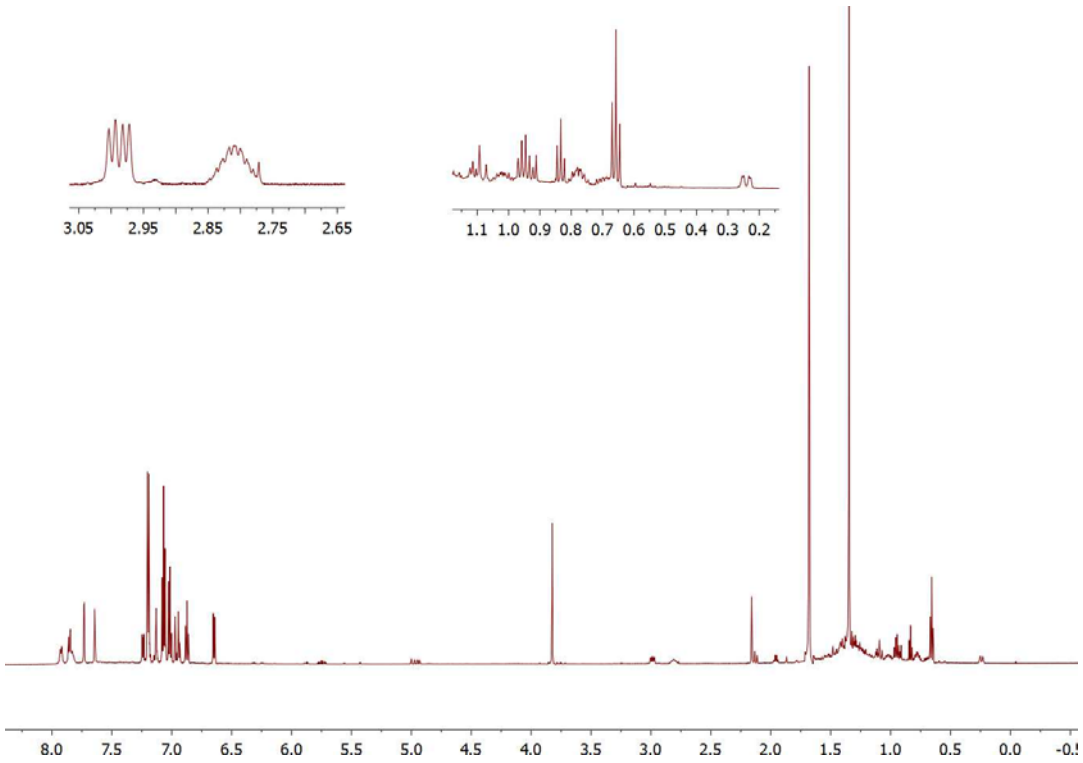


Figure S14: ^{1}H NMR (C_6D_5Cl, 25 °C) of the metallacyclic complex **5**.

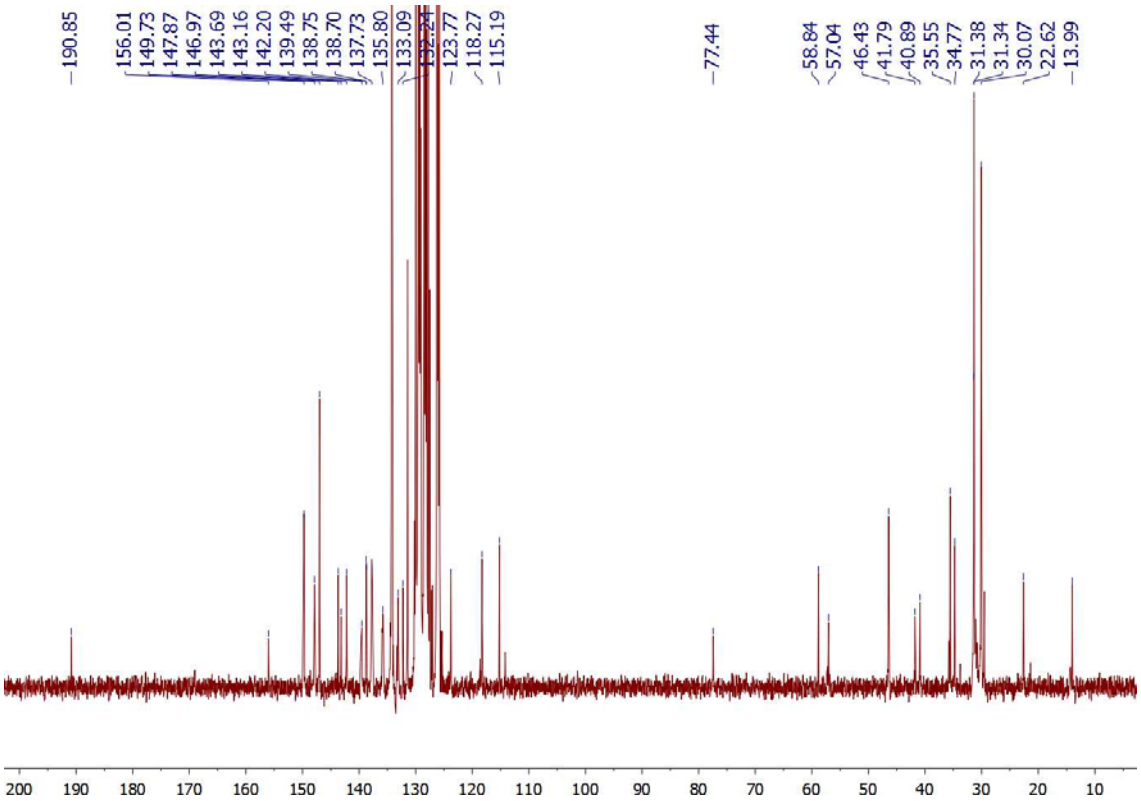


Figure S15: ^{13}C NMR (C_6D_5Cl, 25 °C) of the metallacyclic complex **5**.

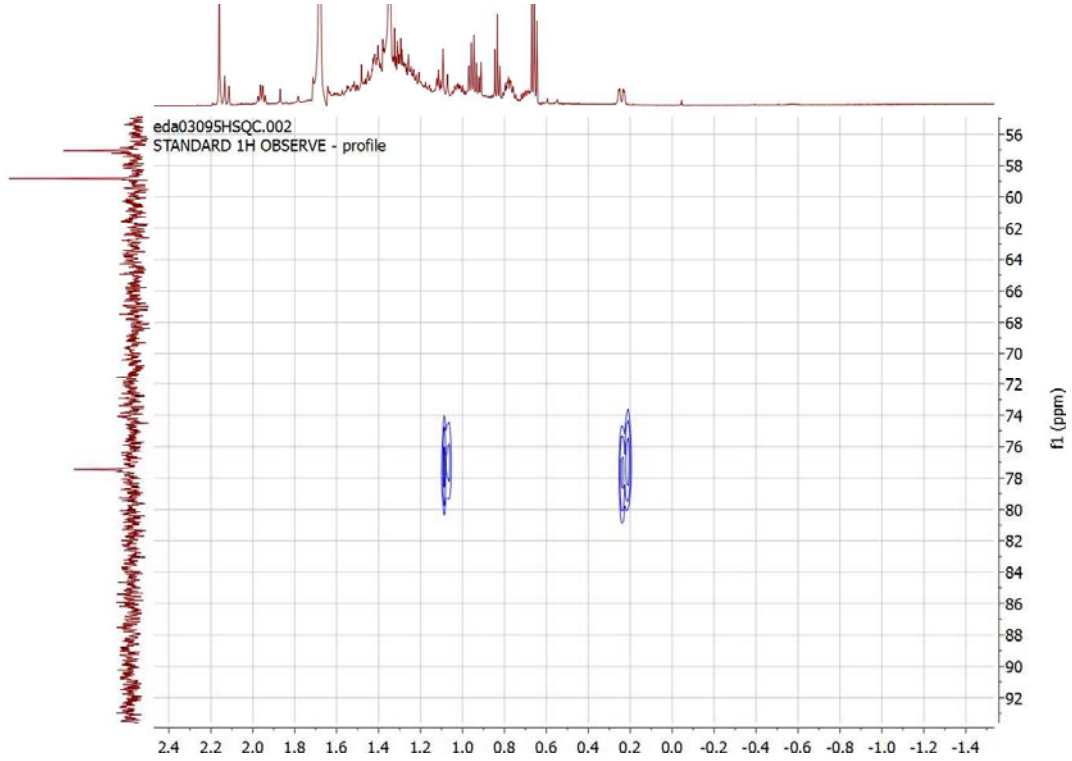


Figure S16: HSQC (C_6D_5Cl, 25 °C) of the metallacyclic complex **5**.

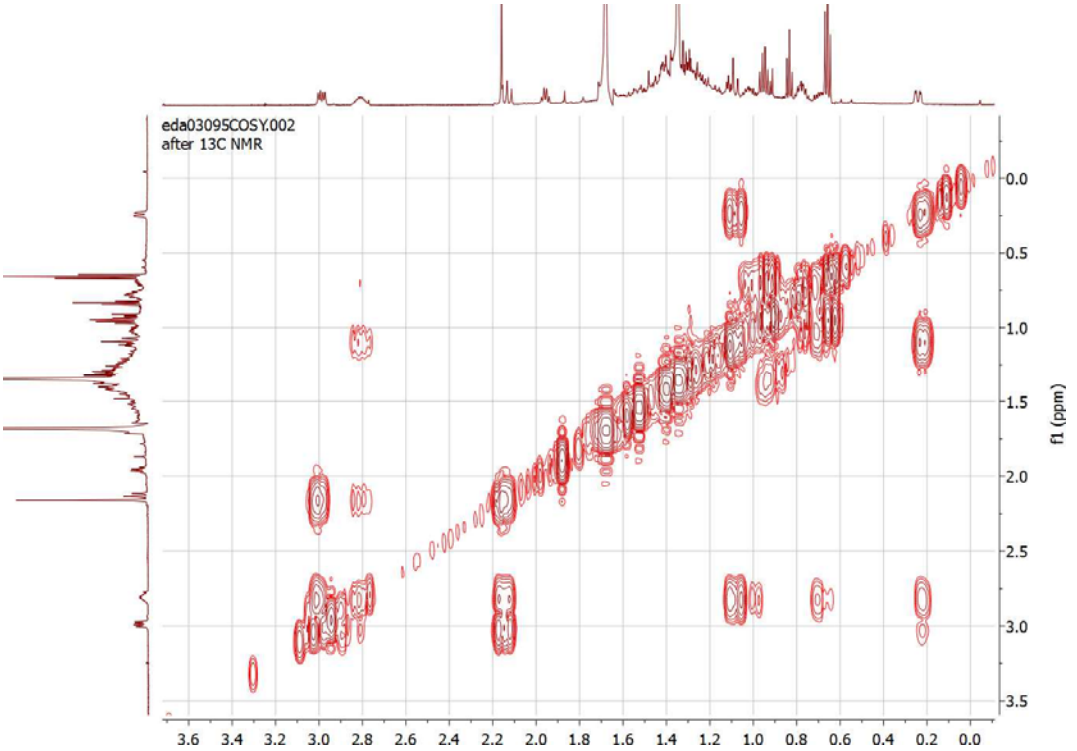


Figure S17: COSY (C_6D_5Cl, 25 °C) of the metallacyclic complex **5**.

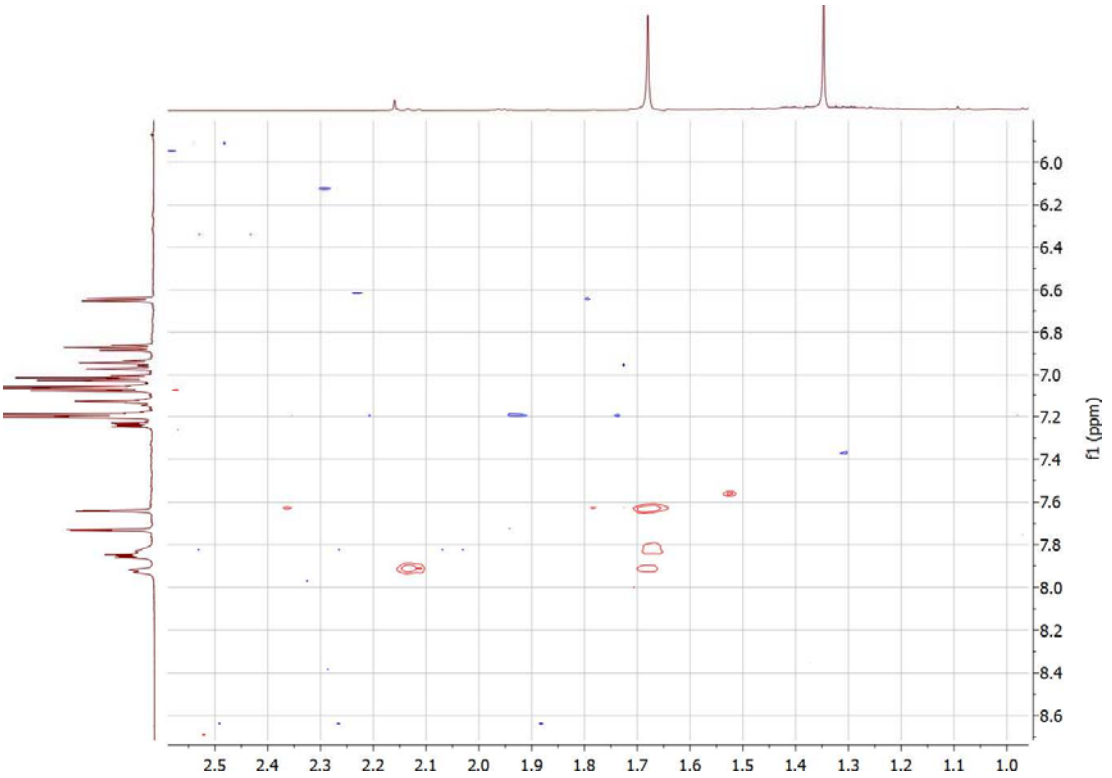


Figure S18: NOESY (C_6D_5Cl, 25 °C) of the metallacyclic complex **5**.

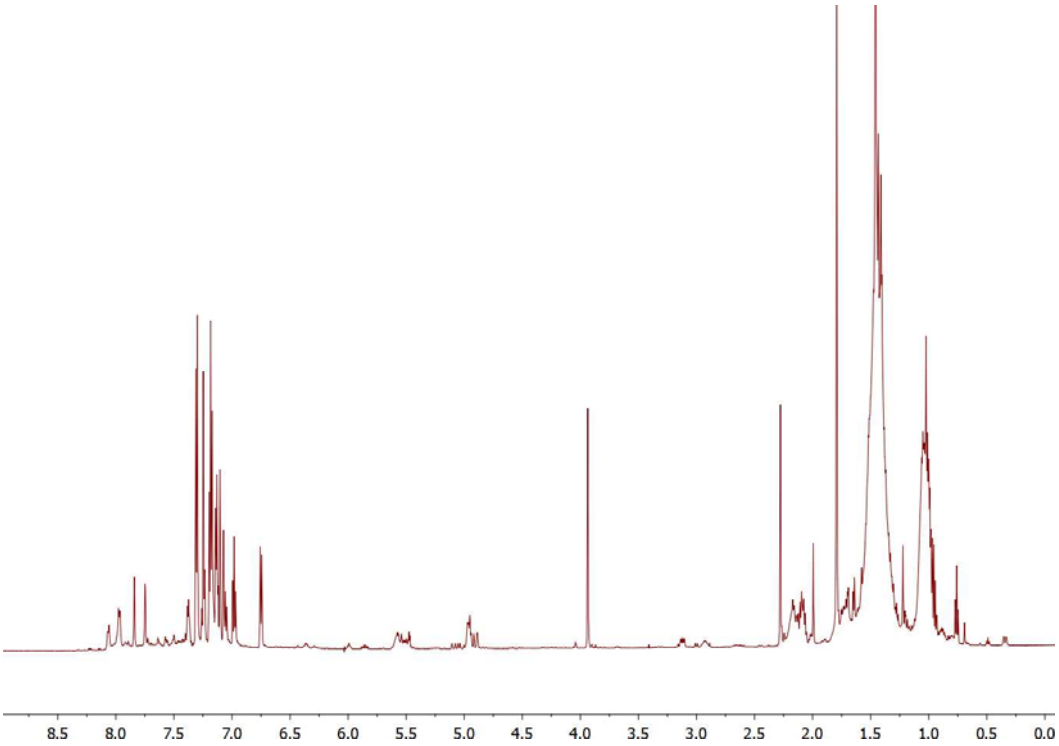


Figure S19: ^1H NMR (C_6D_5Cl, 25 °C) of the metallacyclic complex **5** with 10 equiv. of 1-hexene.

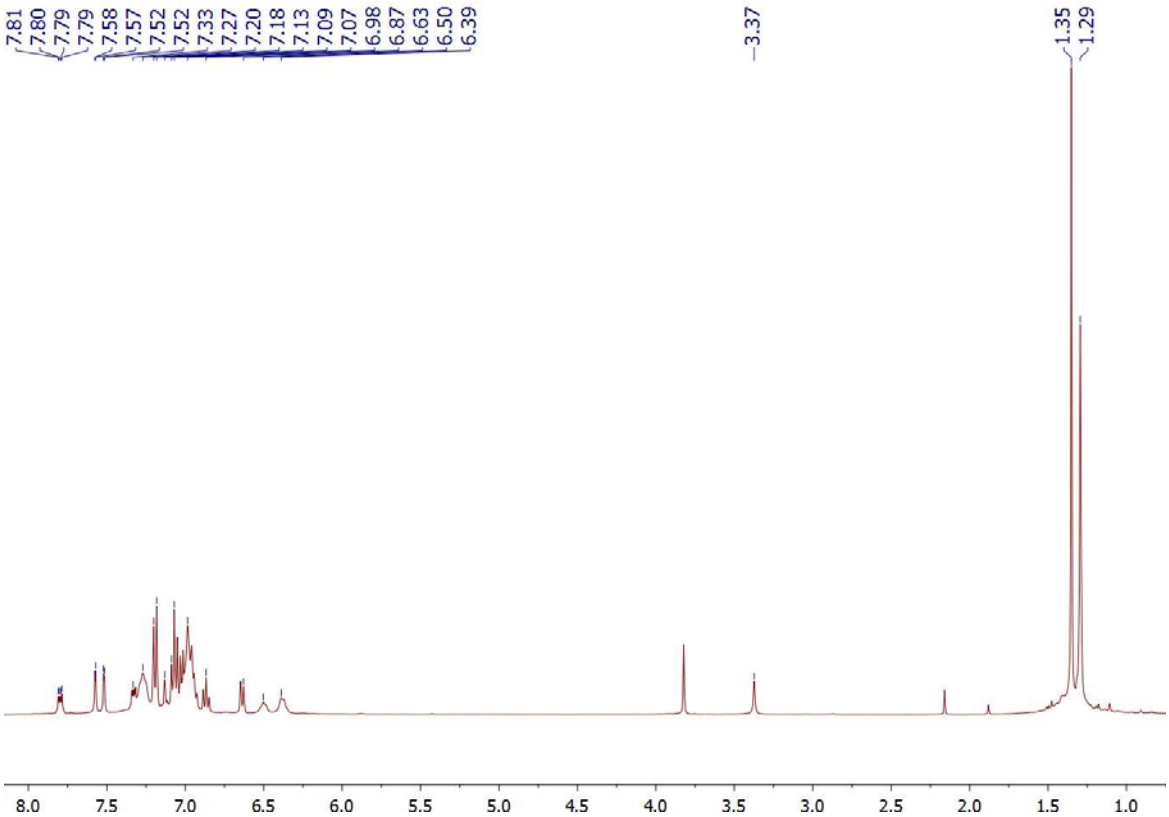


Figure S20: ^{1}H NMR (C_6D_5Cl, 25 °C) of complex **6** (**1**/[Ph_3C][$B(C_6F_5)_4$]/PPh_3).

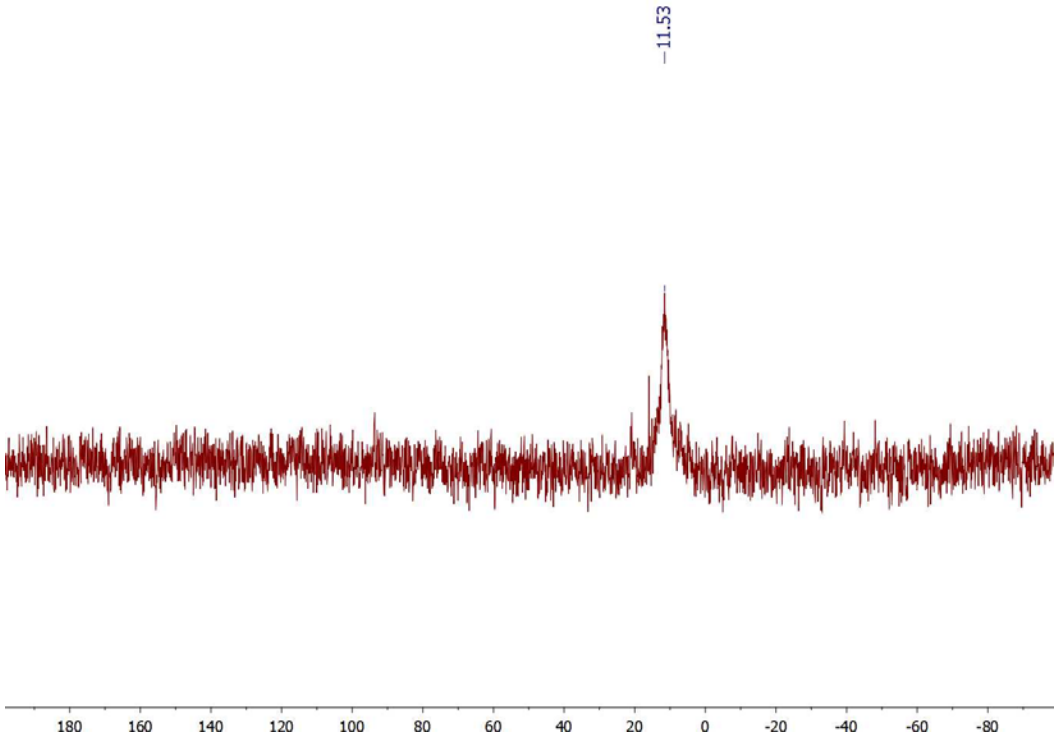


Figure S21: ^{31}P NMR (C_6D_5Cl, 25 °C) of complex **6** (**1**/[Ph_3C][$B(C_6F_5)_4$]/PPh_3).

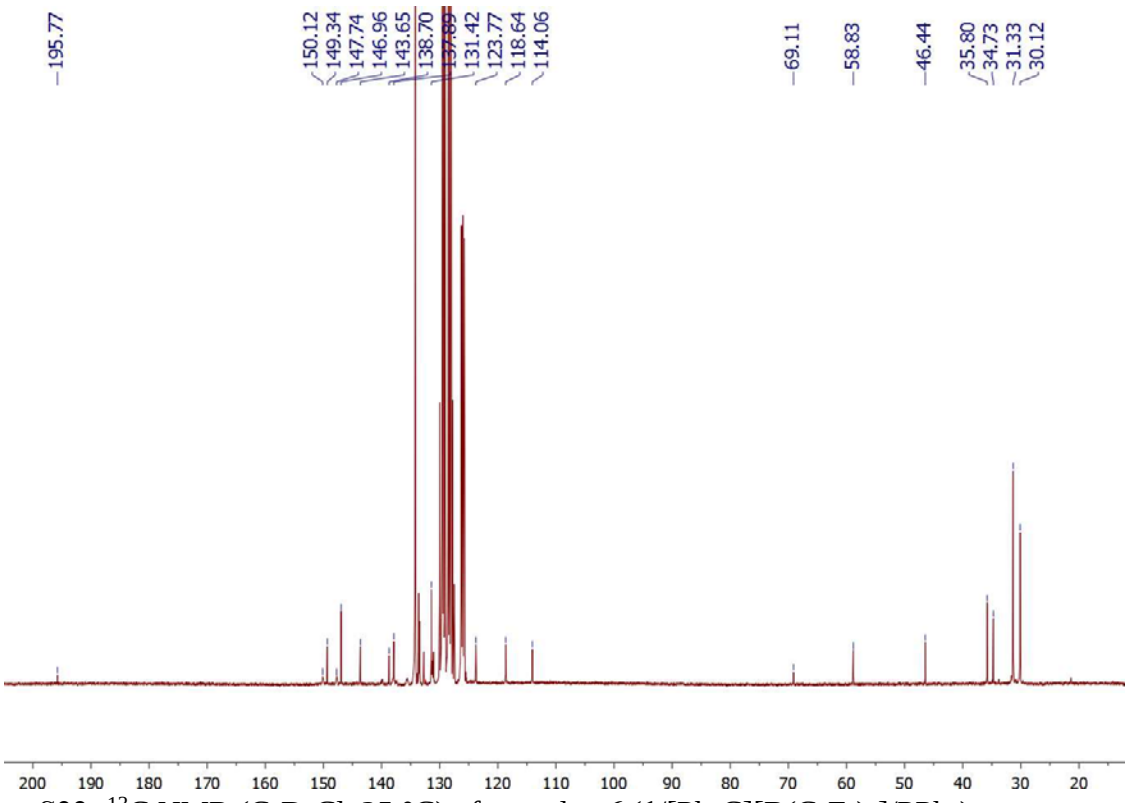


Figure S22: ^{13}C NMR (C_6D_5Cl, 25 °C) of complex **6** (**1**/[Ph_3C][$B(C_6F_5)_4$]/PPh_3).

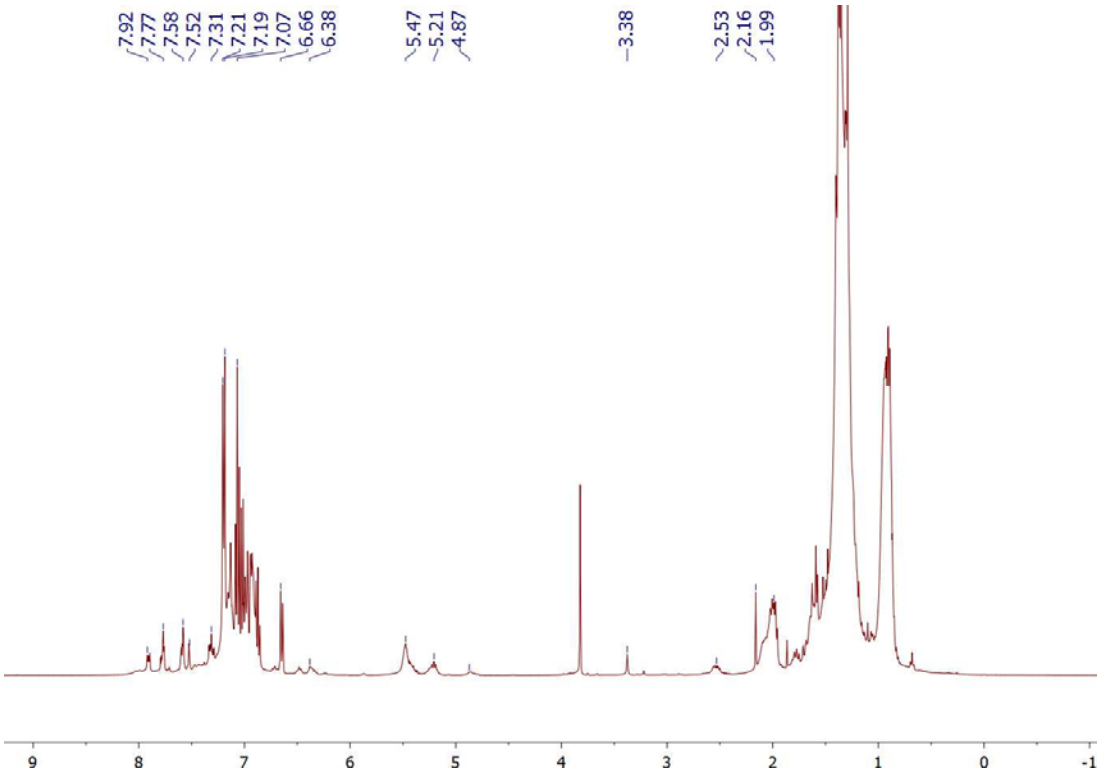


Figure S23: ^{1}H NMR (C_6D_5Cl, 25 °C) of complex **6** with 10 equiv. of 1-hexene.

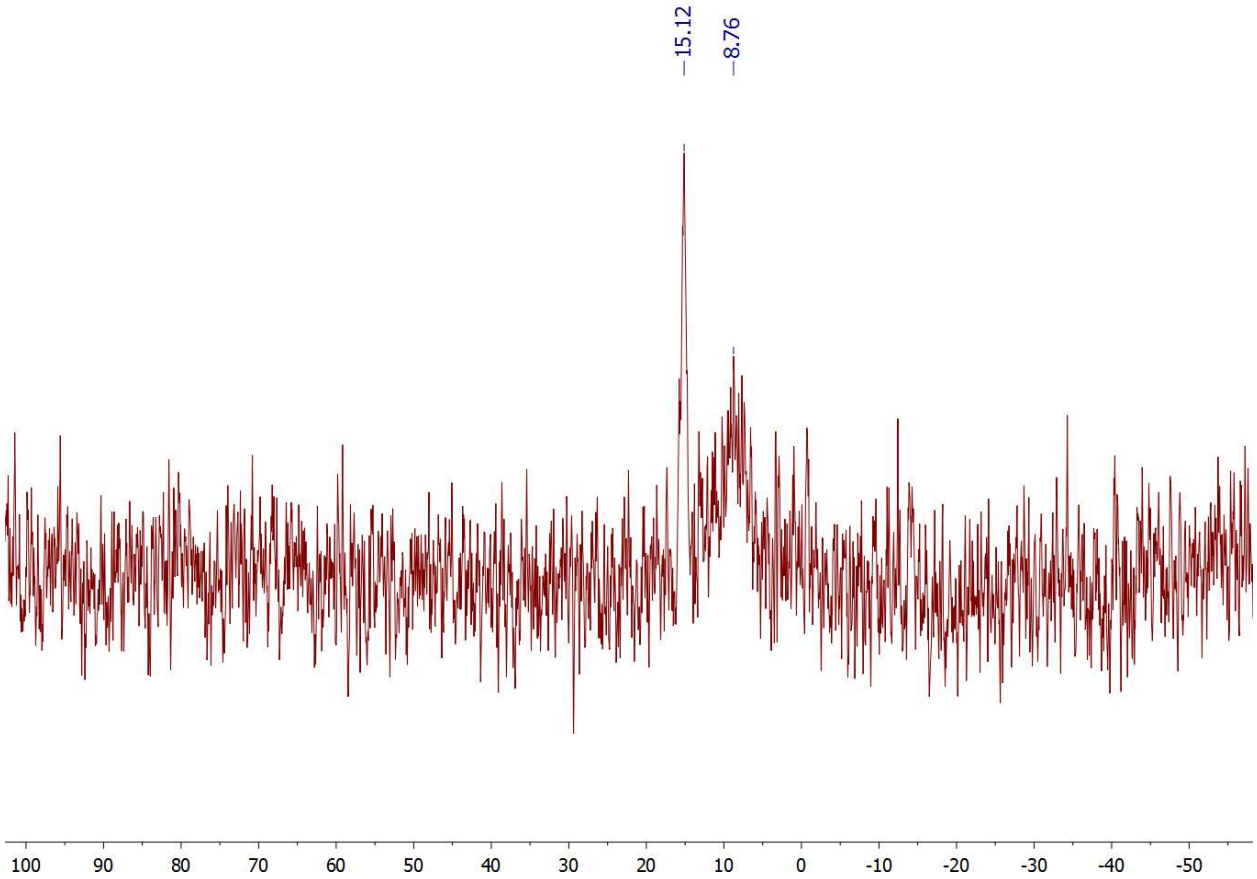


Figure S24: ^{31}P NMR (C_6D_5Cl, 25 °C) of complex **6** with 10 equiv. of 1-hexene.

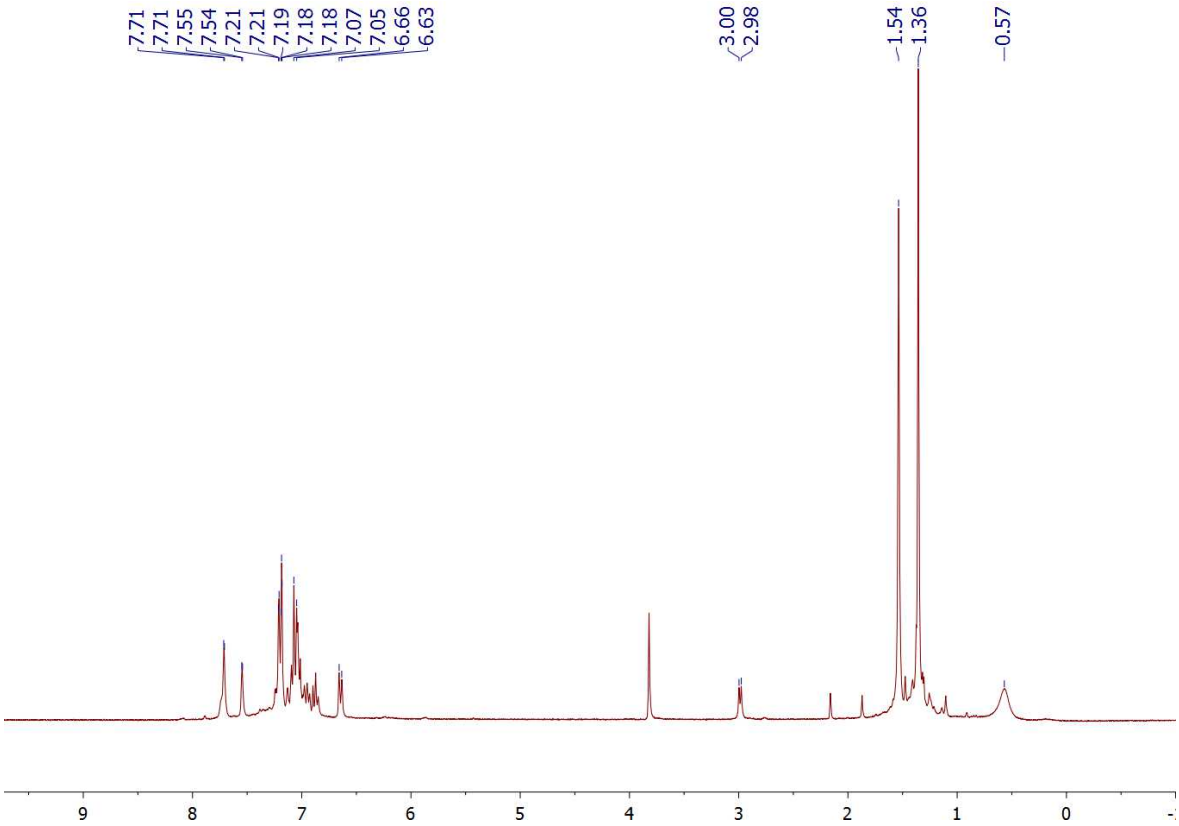


Figure S25: ^{1}H NMR (C_6D_5Cl, 25 °C) of complex **3** (**1**/[Ph_3C][$B(C_6F_5)_4$]/PMe_3).

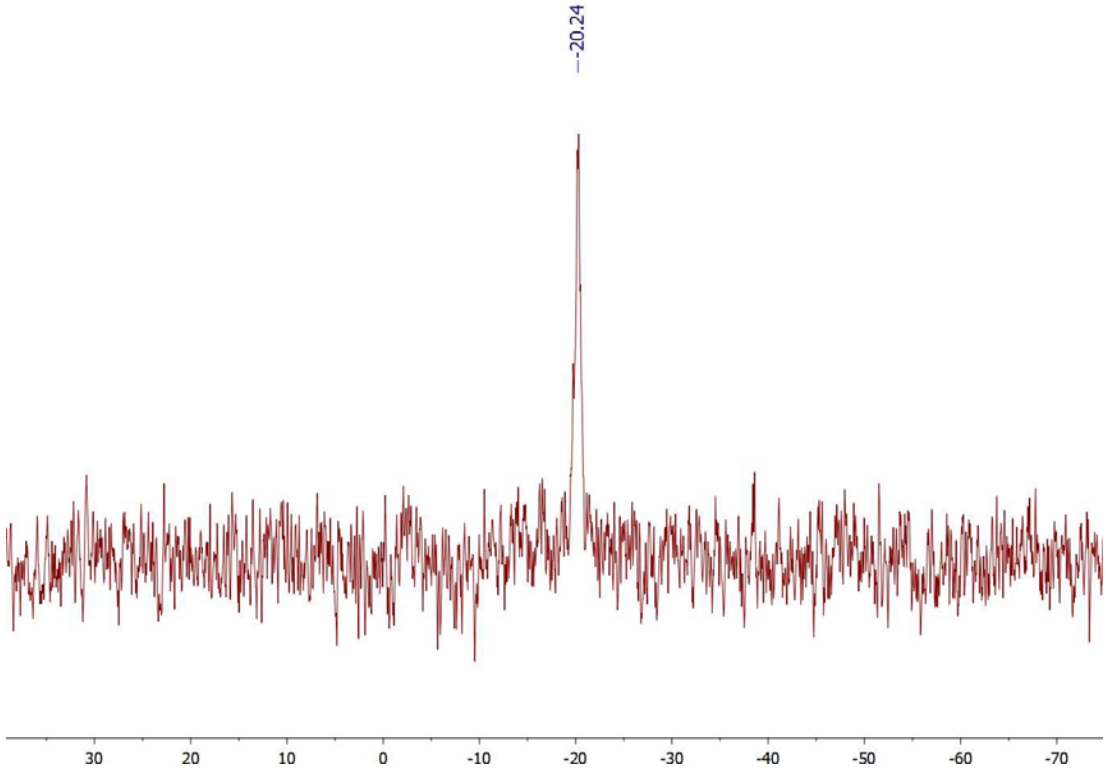


Figure S26: ^{31}P NMR (C_6D_5Cl, 25 °C) of complex **3** (**1**/[Ph_3C][$B(C_6F_5)_4$]/PMe_3).

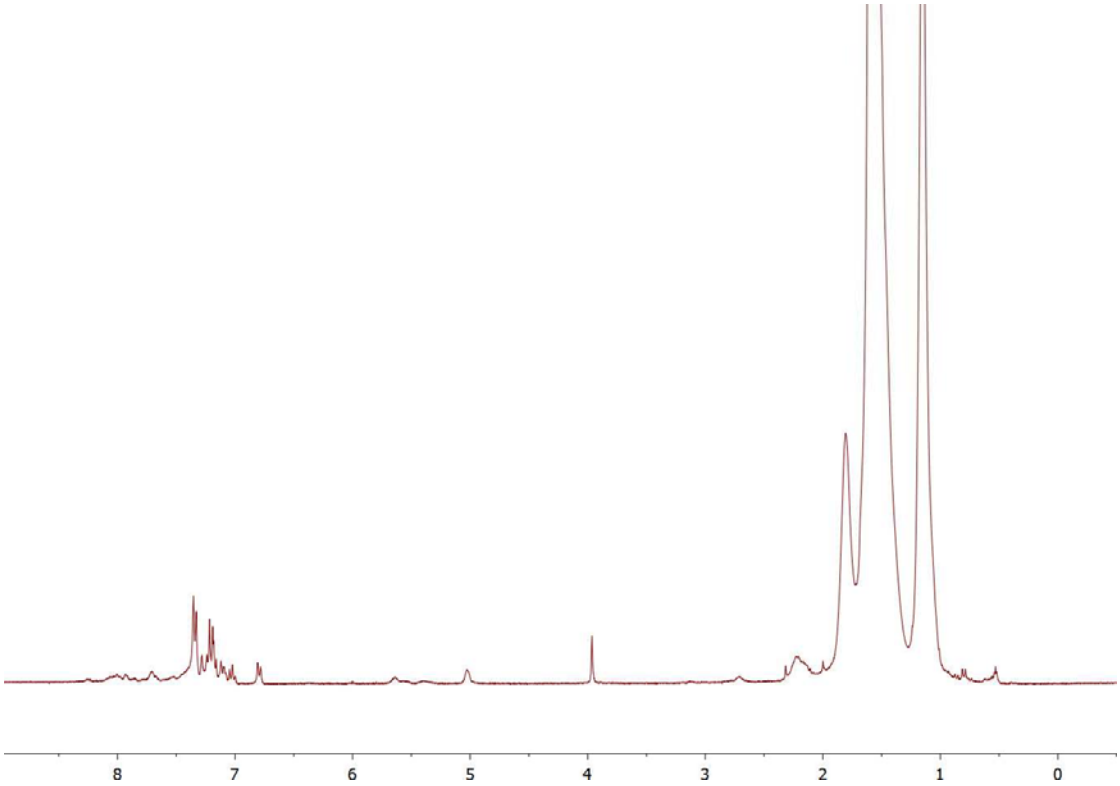


Figure S27: ^{1}H NMR (C_6D_5Cl, 25 °C) of complex **3** with 10 equiv. of 1-hexene.

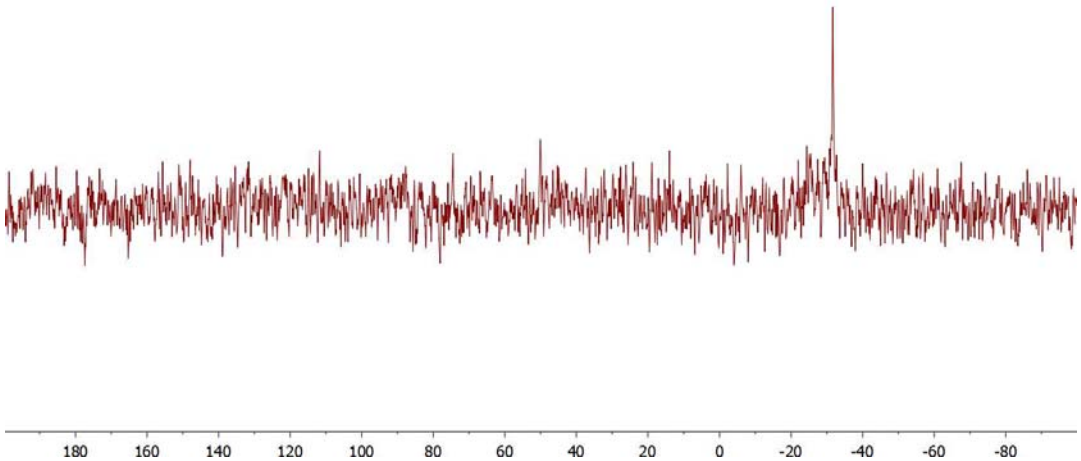


Figure S28: ^{31}P NMR (C_6D_5Cl, 25 °C) of complex **3** with 10 equiv. 1-hexene.

Characterization of the polymers/oligomers:

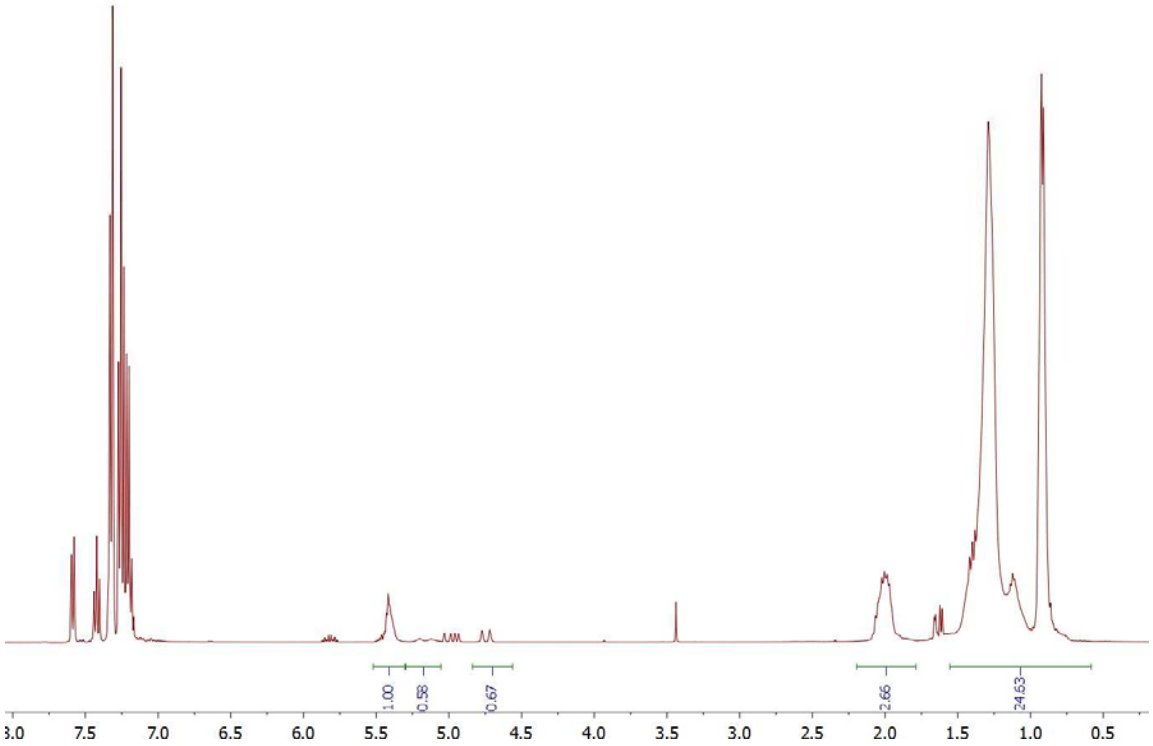


Figure S29: ^{1}H NMR ($CDCl_3$) of oligo(1-hexene) obtained using **1**/[Ph_3C][$B(C_6F_5)_4$].

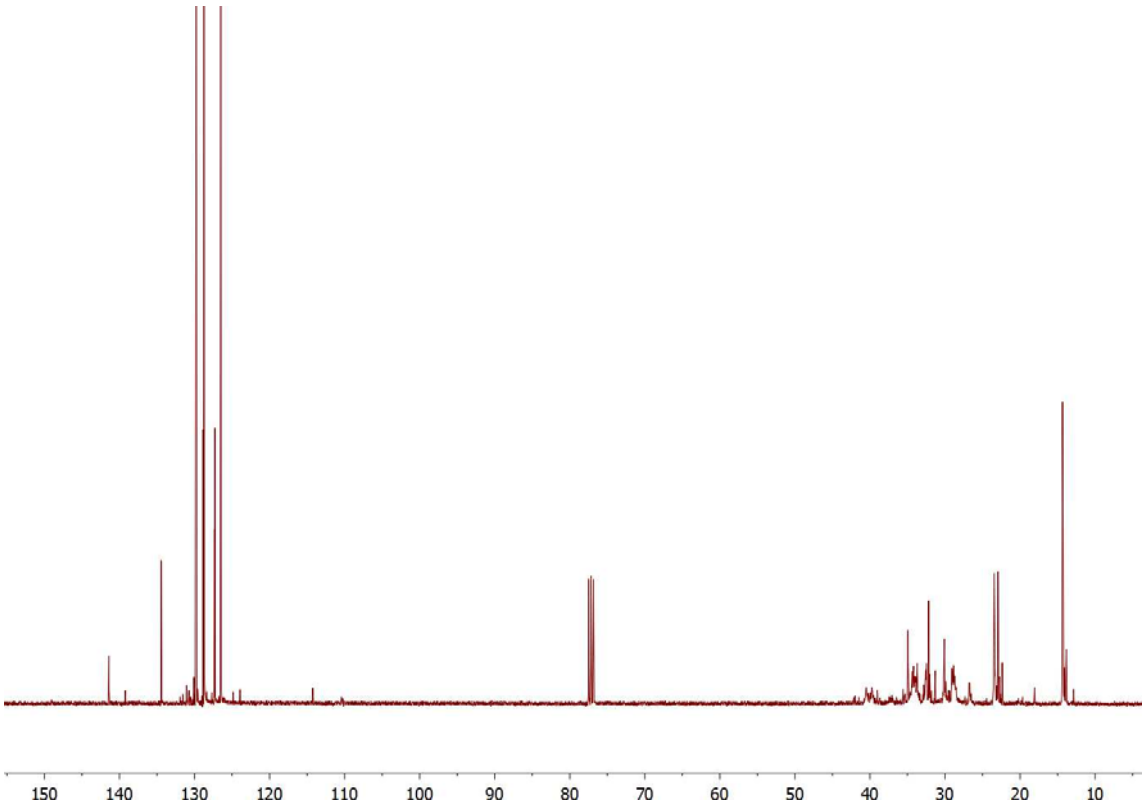


Figure S30: ^{13}C NMR ($CDCl_3$) of oligo(1-hexene) obtained using **1**/[Ph_3C][$B(C_6F_5)_4$].

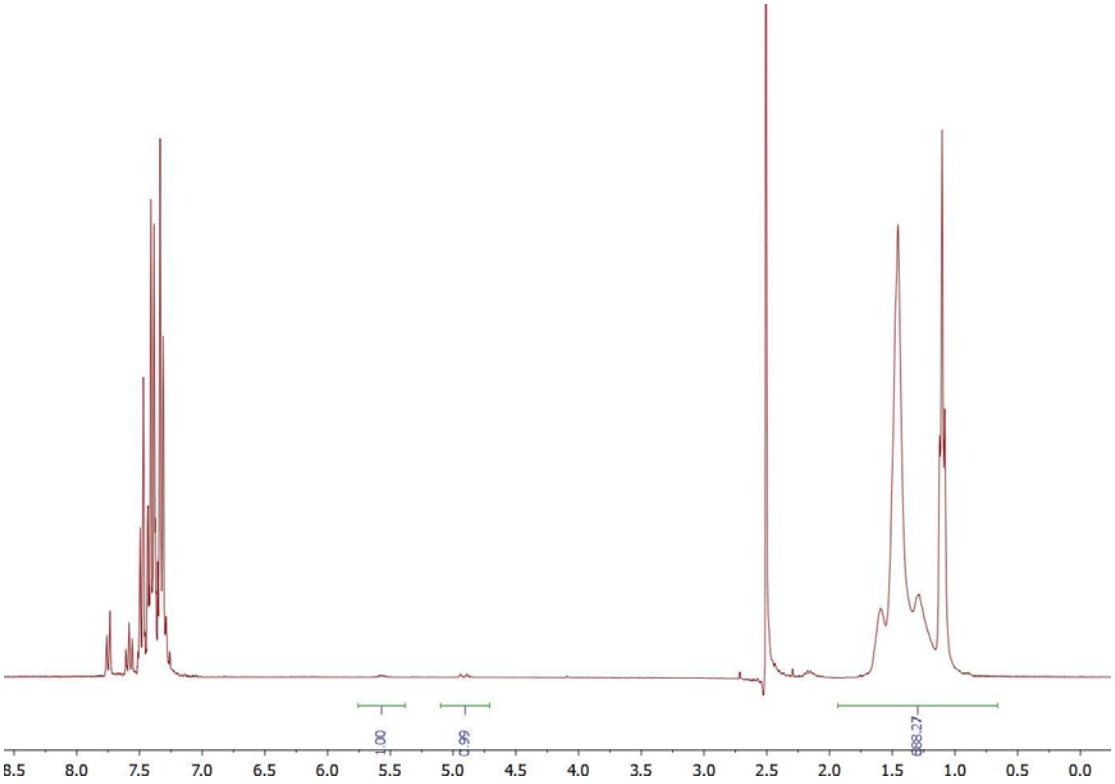


Figure S31: ^{1}H NMR ($CDCl_3$) of poly(1-hexene) obtained using **1**/[Ph_3C][$B(C_6F_5)_4$]/PMe_3.

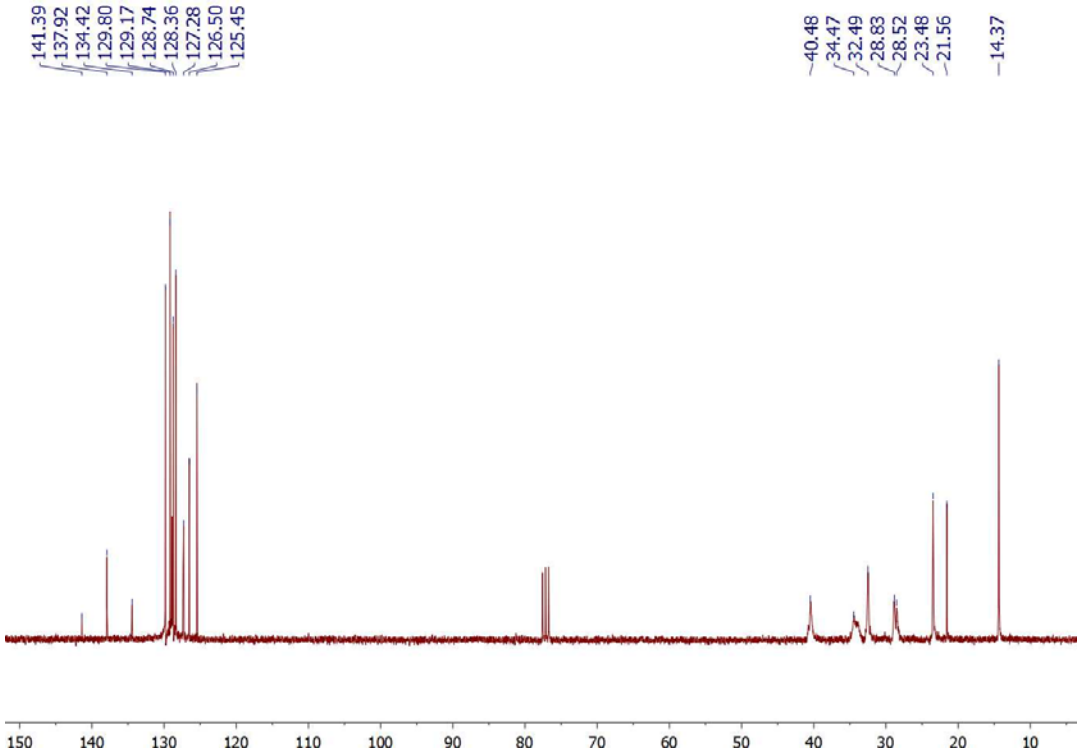


Figure S32: ^{13}C NMR ($CDCl_3$) of poly(1-hexene) obtained using **1**/[Ph_3C][$B(C_6F_5)_4$]/PMe_3.

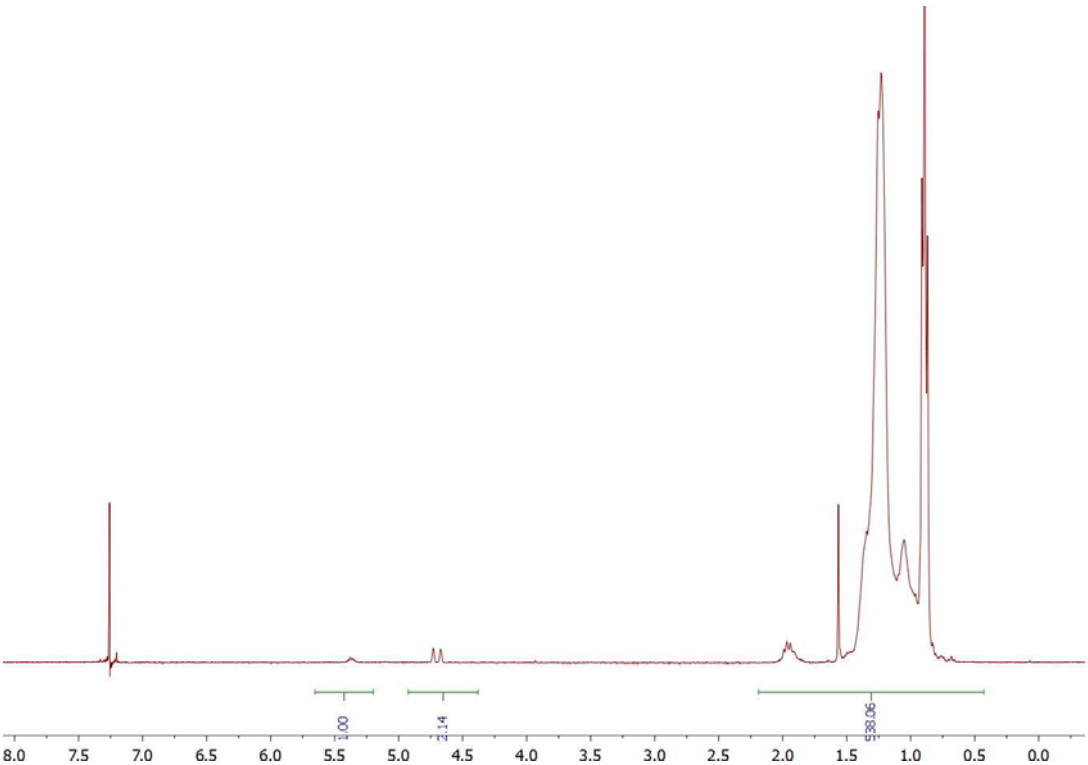


Figure S33: ^{1}H NMR ($CDCl_3$) of poly(1-hexene) obtained using **1**/[Ph_3C][$B(C_6F_5)_4$]/PEt_3.

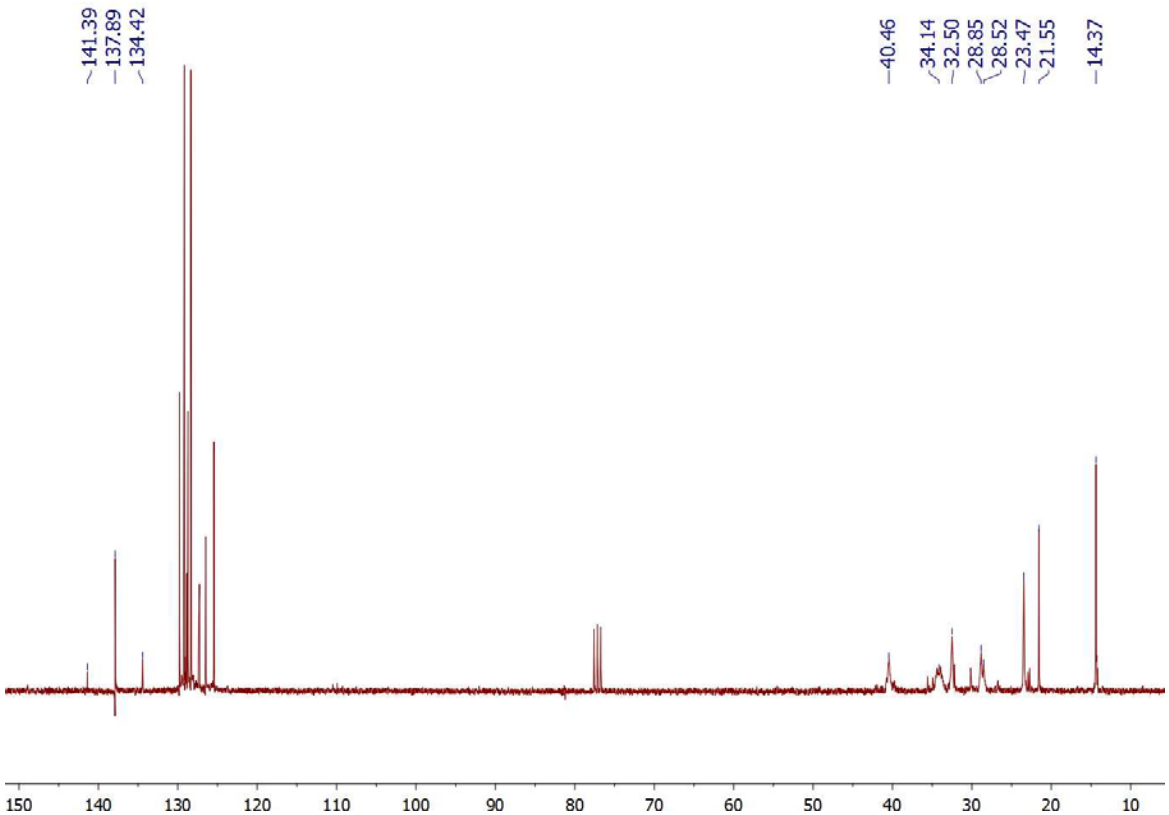


Figure S34: ^{13}C NMR ($CDCl_3$) of poly(1-hexene) obtained using **1**/[Ph_3C][$B(C_6F_5)_4$]/PEt_3.

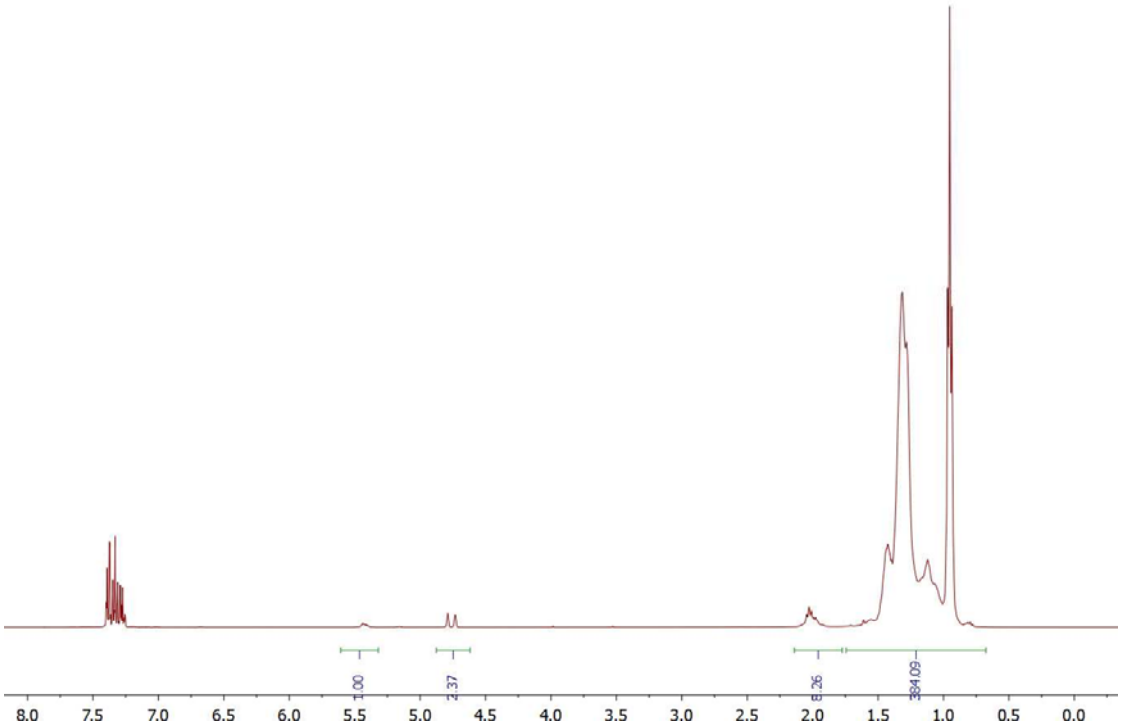


Figure S35: ^{1}H NMR ($CDCl_3$) of poly(1-hexene) obtained using **1**/[Ph_3C][$B(C_6F_5)_4$]/PMe_2Ph.

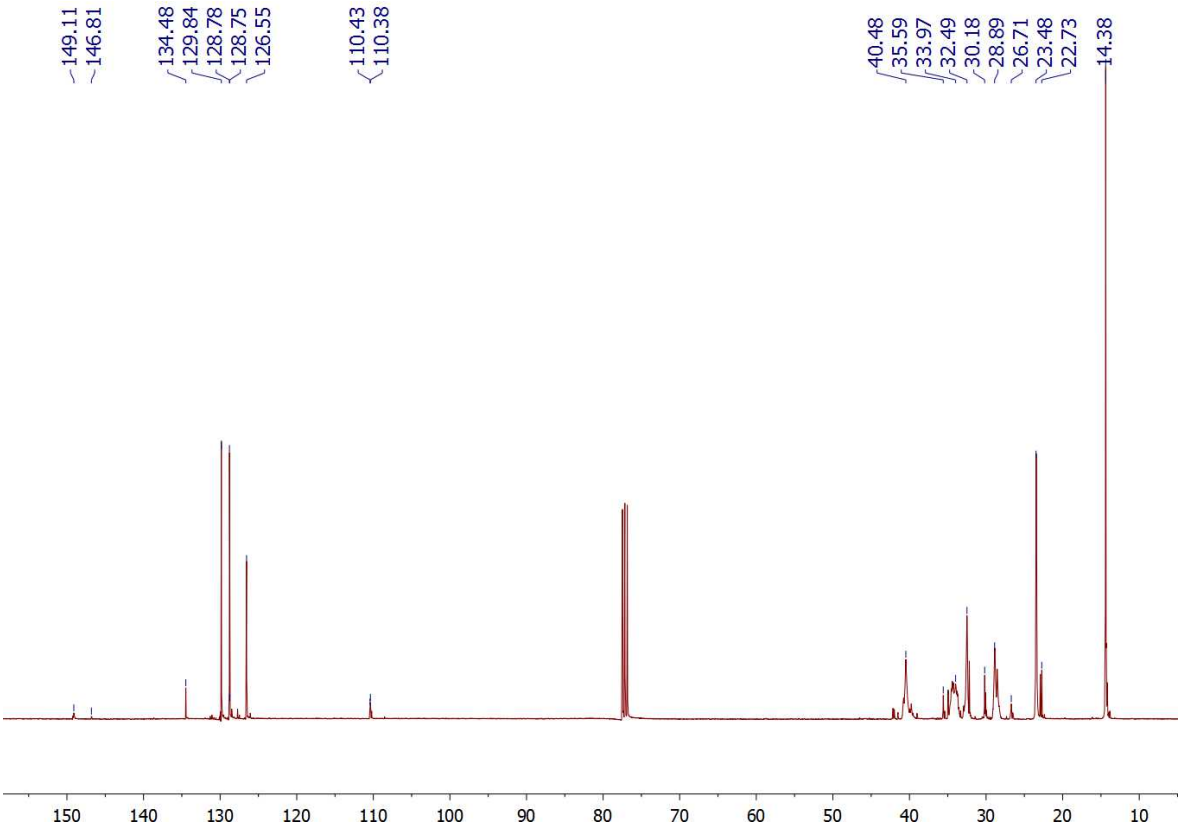


Figure S36: ^{13}C NMR ($CDCl_3$) of poly(1-hexene) obtained using **1**/[Ph_3C][$B(C_6F_5)_4$]/PMe_2Ph.

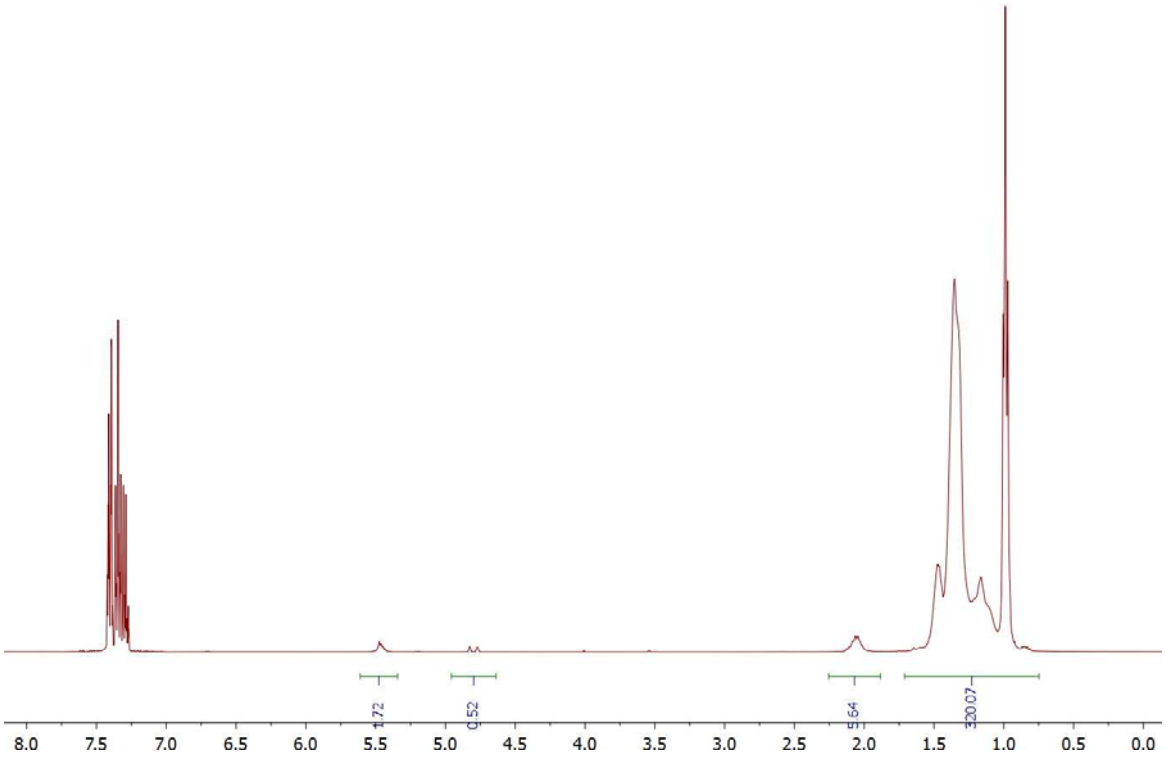


Figure S37: ^{1}H NMR ($CDCl_3$) of poly(1-hexene) obtained using **1**/[Ph_3C][$B(C_6F_5)_4$]/$PEtPh_2$.

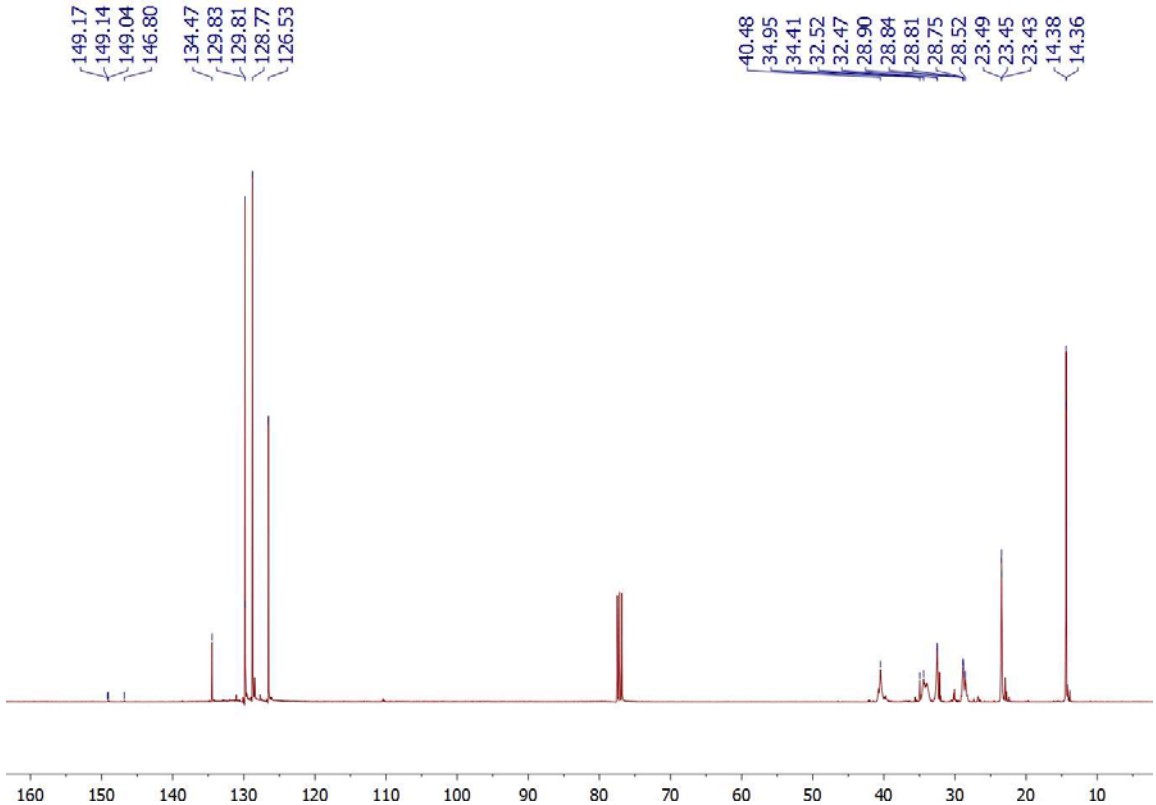


Figure S38: ^{13}C NMR ($CDCl_3$) of poly(1-hexene) obtained using **1**/[Ph_3C][$B(C_6F_5)_4$]/$PEtPh_2$.

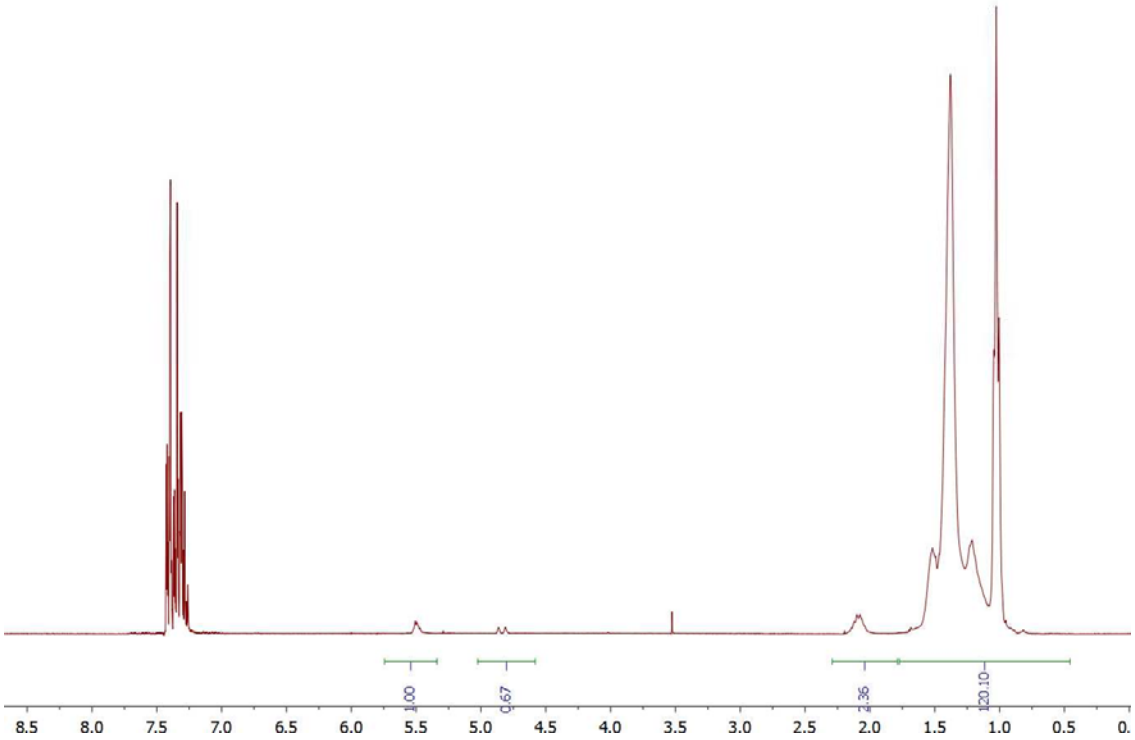


Figure S39: ^{1}H NMR ($CDCl_3$) of poly(1-hexene) obtained using **1**/[Ph_3C][$B(C_6F_5)_4$]/$PMePh_2$.

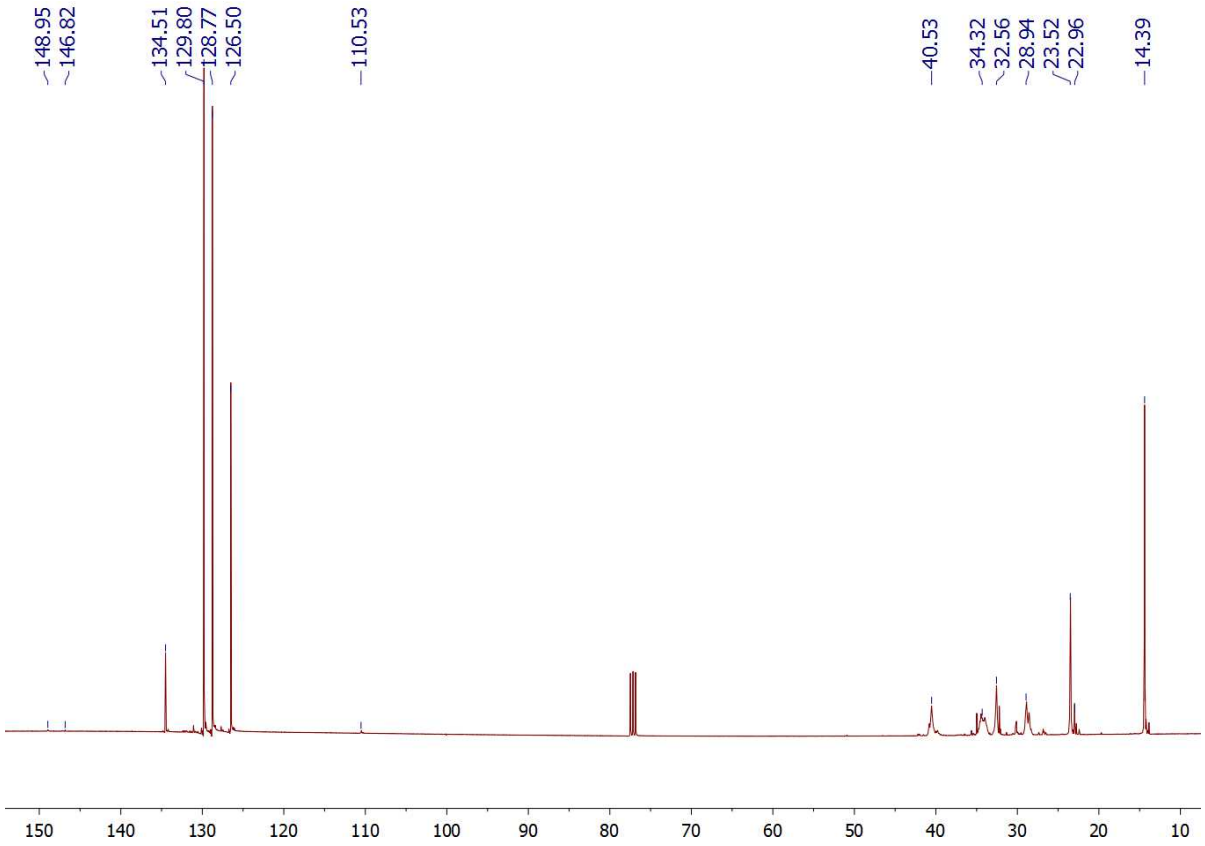
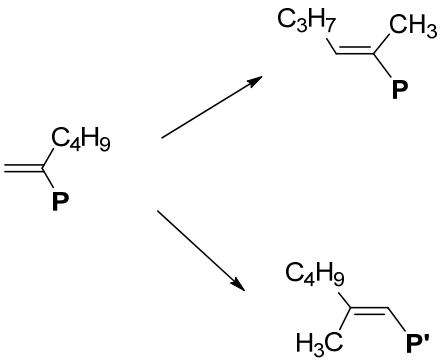


Figure S40: ^{13}C NMR ($CDCl_3$) of poly(1-hexene) obtained using **1**/[Ph_3C][$B(C_6F_5)_4$]/$PMePh_2$.

Isomerization (chain walking process):



a) b)

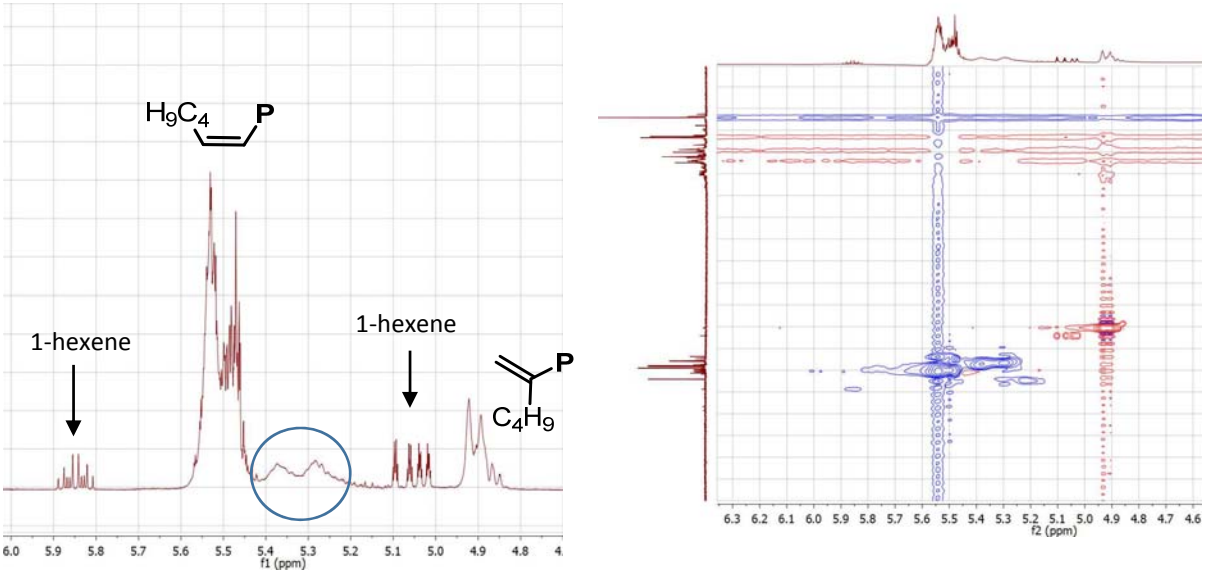


Figure S41: a) Selected range of the ^{1}H NMR ($CDCl_3$) of the oligo(1-hexene) obtained using **1**/[Ph_3C][$B(C_6F_5)_4$]. b) HSQC experiment.

Reaction profile at higher dilution:

In the glove box, a mixture of $[Ph_3C][B(C_6F_5)_4]$ (5.7 mg, 0.0063 mmol) and complex **1** (5 mg, 0.0063 mmol) in chlorobenzene-d_5 (**1.2 mL**) was stored in a NMR tube with a J-Young valve. Then addition of 1-hexene (0.26 g, 0.00315 mol) was realized at room temperature and a chronometer was started in order to take into account the elapsed time before the first NMR acquisition. An array of 360 steps was performed using the Varian parameters "pad" at 25 ºC (time delay: 35s, acquisition time: 25 s, number of scans: 8, first pad set as 0).

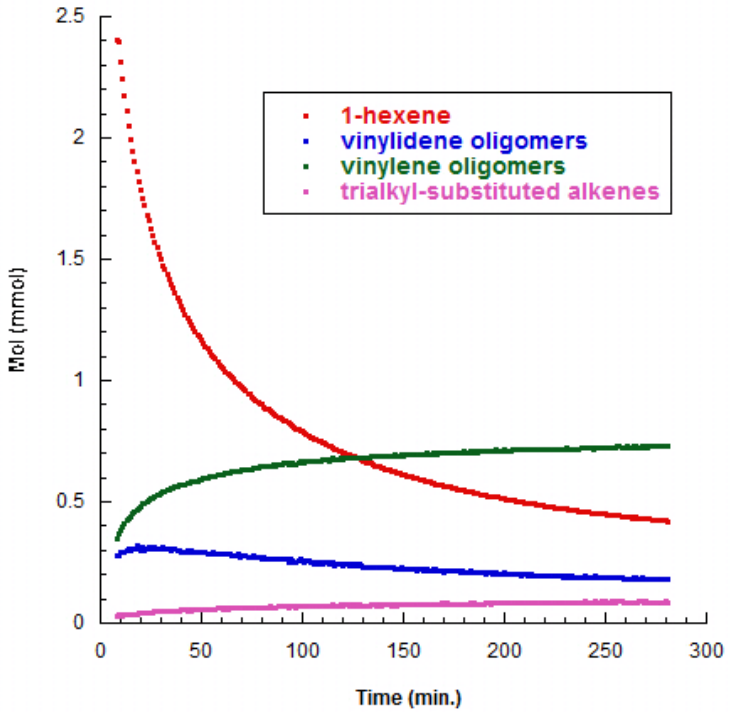


Figure S42: Reaction profile of 1-hexene oligomerization with **1**/$[Ph_3C][B(C_6F_5)_4]$. Conditions: 500 equiv. 1-hexene, **1**/$[Ph_3C][B(C_6F_5)_4]$: 1/1, chlorobenzene (**1.2 mL**), 25 ºC.

Dynamic NMR of complex 4 :

The determination of the exchange constant k at different temperatures have been realized with the DNMR software of Topspin 1.3..

a) Simulation on the ^{1}H NMR spectrum:

T (Kelvin)	k (s^{-1})
263	30
273	140
283	380
293	700
303	1400
313	2800
323	6000

Table 1: Determination of the exchange constant at different temperatures.

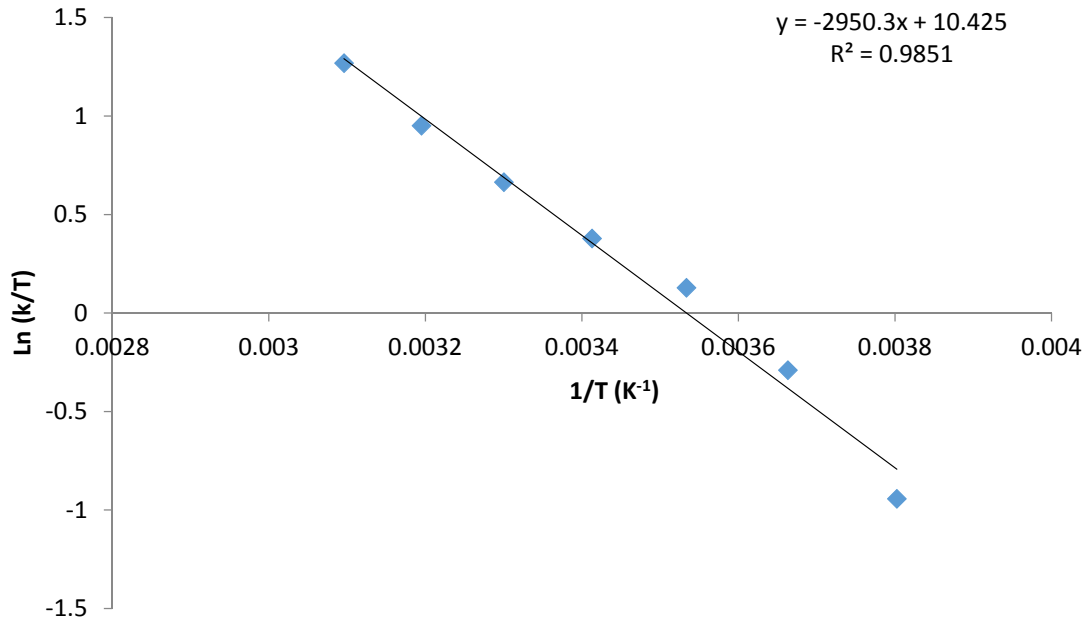


Figure S43: Eyring plot.

According to the Eyring plot:

$$-\frac{\Delta H}{4{,}58} = -2950{,}3 \qquad \Delta H = 13512 \text{ cal/mol}$$

$$\frac{\Delta S}{4{,}58} + 10{,}32 = 10{,}43 \qquad \Delta S = 0{,}50 \text{ cal/mol}$$

At 293K: **ΔG** = 13512 – 293 (0,50) = **13,4 Kcal/mol**

b) Simulation on the ^{31}P NMR spectrum:

T (Kelvin)	k (s^{-1})
263	25
273	120
283	350
293	700
303	2000
313	4000
323	8000

Table 2: Determination of the exchange constant at different temperatures.

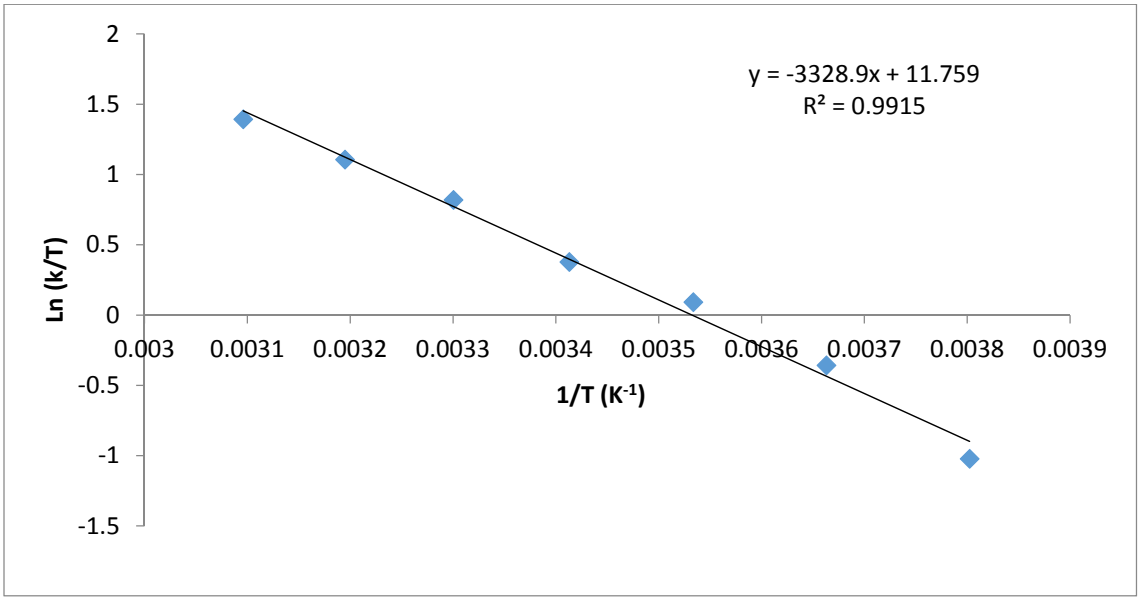


Figure S44: Eyring plot.

$$-\frac{\Delta H}{4{,}58} = -3328{,}9 \qquad \Delta H = 15246 \text{ cal/mol}$$

$$\frac{\Delta S}{4{,}58} + 10{,}32 = 11{,}76 \qquad \Delta S = 6{,}59 \text{ cal/mol}$$

At 293K: **ΔG** = 15246 – 293 (6.59) = **13,3 Kcal/mol**

Crystallographic data:

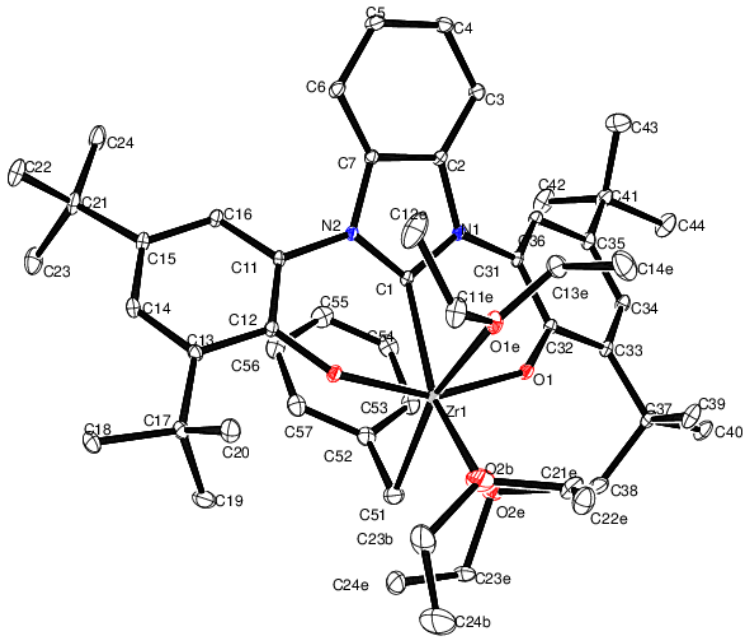


Figure S45: Molecular structure of complex 2 (CCDC 1402120)**.** The counter anion ($B(C_6F_5)_4$) and the hydrogens were omitted for clarity.

Low-temperature diffraction data (ϕ-and ω-scans) were collected on a Bruker AXS D8 VENTURE KAPPA diffractometer coupled to a PHOTON 100 CMOS detector with Mo K_α radiation (λ = 0.71073 Å) from an IμS micro-source for the structure of compound **2**. The structure was solved by direct methods using SHELXS[i] and refined against F^2 on all data by full-matrix least squares with SHELXL-2014[ii] using established refinement techniques.[iii] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). All disordered atoms were refined with the help of similarity restraints on the 1,2- and 1,3-distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters.

Compound **2** crystallizes in the triclinic space group P-1 with one molecule in the asymmetric unit along with pentane and diethyl ether. One of the diethyl ether molecules bound to the zirconium was disordered over two positions. One of the diethyl ether molecules in the crystal is located near a crystallographic inversion center and disordered accordingly. The disordered ether bound to the Zn and the two outer sphere ether molecules were refined with the help of similarity restraints on the 1,2- and 1,2- distances. The structure also contains two solvent accessible channels which were modeled as continuous string of pentane molecules in which adjacent pentane molecules were separated by one vacant position. As such each atom was modeled as 5/6 of an atom. One of the solvent strings was additionally modeled as a mixture of two mutually exclusive chains of pentane. The occupancy of the two chains refined freely to 0.546(7):0.287(7), which takes into account the 5/6 population of each atomic position. There is significant elongation in the ellipsoids in both pentane chains, however, refinement of additional disorder did not converge.

Table 3: Crystal data and structure refinement for P14042.

Empirical formula	C88.34 H106 B F20 N2 O5.50 Zr	
Formula weight	1765.80	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.4145(9) Å	α= 110.410(2)°.
	b = 18.8131(12) Å	β= 103.088(3)°.
	c = 21.1906(15) Å	γ = 103.450(2)°.
Volume	4246.7(5) $Å^3$	
Z	2	
Density (calculated)	1.381 Mg/m^3	
Absorption coefficient	0.226 mm^{-1}	
F(000)	1838	
Crystal size	0.500 x 0.350 x 0.150 mm^3	
Theta range for data collection	2.391 to 30.508°.	
Index ranges	-17<=h<=17, -26<=k<=26, -30<=l<=30	
Reflections collected	166089	
Independent reflections	25914 [R(int) = 0.0571]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7467 and 0.6311	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	25914 / 417 / 1188	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.0521, wR2 = 0.1274	
R indices (all data)	R1 = 0.0671, wR2 = 0.1355	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.892 and -1.486 e.$Å^{-3}$	

Table 4: Bond lengths [Å] and angles [°] for complex 2.

Zr(1)-O(1)	1.9890(12)	C(15)-C(21)	1.536(2)
Zr(1)-O(2)	2.0003(12)	C(21)-C(24)	1.528(3)
Zr(1)-C(51)	2.300(2)	C(21)-C(22)	1.535(3)
Zr(1)-C(1)	2.3011(17)	C(21)-C(23)	1.542(3)
Zr(1)-O(2B)	2.308(12)	C(22)-H(22A)	0.9800
Zr(1)-O(2E)	2.308(4)	C(22)-H(22B)	0.9800
Zr(1)-O(1E)	2.3940(14)	C(22)-H(22C)	0.9800
Zr(1)-C(52)	2.6122(19)	C(23)-H(23A)	0.9800
C(1)-N(2)	1.360(2)	C(23)-H(23B)	0.9800
C(1)-N(1)	1.363(2)	C(23)-H(23C)	0.9800
N(1)-C(2)	1.410(2)	C(24)-H(24A)	0.9800
N(1)-C(31)	1.439(2)	C(24)-H(24B)	0.9800
C(11)-C(12)	1.396(2)	C(24)-H(24C)	0.9800
C(11)-C(16)	1.400(2)	C(16)-H(16)	0.9500
C(11)-N(2)	1.430(2)	O(1)-C(32)	1.348(2)
C(12)-O(2)	1.349(2)	C(2)-C(3)	1.395(2)
C(12)-C(13)	1.423(2)	C(2)-C(7)	1.397(2)
C(13)-C(14)	1.394(2)	C(3)-C(4)	1.391(3)
C(13)-C(17)	1.533(2)	C(3)-H(3)	0.9500
C(17)-C(20)	1.538(3)	C(4)-C(5)	1.399(3)
C(17)-C(18)	1.539(3)	C(4)-H(4)	0.9500
C(17)-C(19)	1.539(3)	C(5)-C(6)	1.384(3)
C(18)-H(18A)	0.9800	C(5)-H(5)	0.9500
C(18)-H(18B)	0.9800	C(6)-C(7)	1.396(2)
C(18)-H(18C)	0.9800	C(6)-H(6)	0.9500
C(19)-H(19A)	0.9800	C(7)-N(2)	1.401(2)
C(19)-H(19B)	0.9800	C(31)-C(36)	1.390(2)
C(19)-H(19C)	0.9800	C(31)-C(32)	1.410(2)
C(20)-H(20A)	0.9800	C(32)-C(33)	1.412(2)
C(20)-H(20B)	0.9800	C(33)-C(34)	1.397(2)
C(20)-H(20C)	0.9800	C(33)-C(37)	1.538(2)
C(14)-C(15)	1.399(3)	C(37)-C(39)	1.535(3)
C(14)-H(14)	0.9500	C(37)-C(38)	1.538(3)
C(15)-C(16)	1.384(2)	C(37)-C(40)	1.538(3)

C(38)-H(38A)	0.9800	C(55)-H(55)	0.9500
C(38)-H(38B)	0.9800	C(56)-C(57)	1.388(3)
C(38)-H(38C)	0.9800	C(56)-H(56)	0.9500
C(39)-H(39A)	0.9800	C(57)-H(57)	0.9500
C(39)-H(39B)	0.9800	O(1E)-C(11E)	1.455(2)
C(39)-H(39C)	0.9800	O(1E)-C(13E)	1.461(2)
C(40)-H(40A)	0.9800	C(11E)-C(12E)	1.513(4)
C(40)-H(40B)	0.9800	C(11E)-H(11A)	0.9900
C(40)-H(40C)	0.9800	C(11E)-H(11B)	0.9900
C(34)-C(35)	1.398(3)	C(12E)-H(12A)	0.9800
C(34)-H(34)	0.9500	C(12E)-H(12B)	0.9800
C(35)-C(36)	1.391(2)	C(12E)-H(12C)	0.9800
C(35)-C(41)	1.532(2)	C(13E)-C(14E)	1.512(3)
C(41)-C(44)	1.534(3)	C(13E)-H(13A)	0.9900
C(41)-C(42)	1.534(3)	C(13E)-H(13B)	0.9900
C(41)-C(43)	1.536(3)	C(14E)-H(14A)	0.9800
C(42)-H(42A)	0.9800	C(14E)-H(14B)	0.9800
C(42)-H(42B)	0.9800	C(14E)-H(14C)	0.9800
C(42)-H(42C)	0.9800	C(21E)-O(2E)	1.439(4)
C(43)-H(43A)	0.9800	C(21E)-C(22E)	1.502(3)
C(43)-H(43B)	0.9800	C(21E)-O(2B)	1.560(10)
C(43)-H(43C)	0.9800	C(21E)-H(21A)	0.9900
C(44)-H(44A)	0.9800	C(21E)-H(21B)	0.9900
C(44)-H(44B)	0.9800	C(22E)-H(22D)	0.9800
C(44)-H(44C)	0.9800	C(22E)-H(22E)	0.9800
C(36)-H(36)	0.9500	C(22E)-H(22F)	0.9800
C(51)-C(52)	1.474(3)	O(2E)-C(23E)	1.468(4)
C(51)-H(51A)	0.9900	C(23E)-C(24E)	1.496(4)
C(51)-H(51B)	0.9900	C(23E)-H(23D)	0.9900
C(52)-C(53)	1.414(3)	C(23E)-H(23E)	0.9900
C(52)-C(57)	1.415(3)	C(24E)-H(24D)	0.9800
C(53)-C(54)	1.386(3)	C(24E)-H(24E)	0.9800
C(53)-H(53)	0.9500	C(24E)-H(24F)	0.9800
C(54)-C(55)	1.395(3)	O(2B)-C(23B)	1.487(11)
C(54)-H(54)	0.9500	C(23B)-C(24B)	1.493(13)
C(55)-C(56)	1.394(3)	C(23B)-H(23F)	0.9900

C(23B)-H(23G)	0.9900	C(84)-F(13)	1.344(2)
C(24B)-H(24G)	0.9800	C(84)-C(85)	1.379(3)
C(24B)-H(24H)	0.9800	C(85)-F(14)	1.344(2)
C(24B)-H(24I)	0.9800	C(85)-C(86)	1.387(3)
B(1)-C(81)	1.649(3)	C(86)-F(15)	1.349(2)
B(1)-C(91)	1.656(3)	C(91)-C(92)	1.390(2)
B(1)-C(61)	1.656(3)	C(91)-C(96)	1.392(3)
B(1)-C(71)	1.660(3)	C(92)-F(16)	1.353(2)
C(61)-C(62)	1.387(3)	C(92)-C(93)	1.389(3)
C(61)-C(66)	1.395(3)	C(93)-F(17)	1.343(2)
C(62)-F(1)	1.348(2)	C(93)-C(94)	1.373(3)
C(62)-C(63)	1.391(3)	C(94)-F(18)	1.345(2)
C(63)-F(2)	1.348(2)	C(94)-C(95)	1.381(3)
C(63)-C(64)	1.372(3)	C(95)-F(19)	1.345(2)
C(64)-F(3)	1.345(2)	C(95)-C(96)	1.383(3)
C(64)-C(65)	1.376(3)	C(96)-F(20)	1.350(2)
C(65)-F(4)	1.344(2)	O(1S)-C(11S)	1.427(4)
C(65)-C(66)	1.383(3)	O(1S)-C(13S)	1.439(4)
C(66)-F(5)	1.348(2)	C(11S)-C(12S)	1.507(6)
C(71)-C(76)	1.390(3)	C(11S)-H(11C)	0.9900
C(71)-C(72)	1.394(3)	C(11S)-H(11D)	0.9900
C(72)-F(6)	1.356(2)	C(12S)-H(12D)	0.9800
C(72)-C(73)	1.380(3)	C(12S)-H(12E)	0.9800
C(73)-F(7)	1.348(2)	C(12S)-H(12F)	0.9800
C(73)-C(74)	1.376(3)	C(13S)-C(14S)	1.497(5)
C(74)-F(8)	1.344(2)	C(13S)-H(13C)	0.9900
C(74)-C(75)	1.375(3)	C(13S)-H(13D)	0.9900
C(75)-F(9)	1.345(2)	C(14S)-H(14D)	0.9800
C(75)-C(76)	1.385(3)	C(14S)-H(14E)	0.9800
C(76)-F(10)	1.349(2)	C(14S)-H(14F)	0.9800
C(81)-C(86)	1.391(3)	O(2S)-C(23S)	1.491(7)
C(81)-C(82)	1.395(3)	O(2S)-C(21S)	1.492(7)
C(82)-F(11)	1.349(2)	C(21S)-C(22S)	1.485(8)
C(82)-C(83)	1.379(3)	C(21S)-H(21C)	0.9900
C(83)-F(12)	1.344(2)	C(21S)-H(21D)	0.9900
C(83)-C(84)	1.370(3)	C(22S)-H(22G)	0.9800

C(22S)-H(22H)	0.9800	C(14U)-H(14J)	0.9900
C(22S)-H(22I)	0.9800	C(15U)-H(15D)	0.9800
C(23S)-C(24S)	1.484(8)	C(15U)-H(15E)	0.9800
C(23S)-H(23H)	0.9900	C(15U)-H(15F)	0.9800
C(23S)-H(23I)	0.9900	C(21U)-C(22U)	1.458(13)
C(24S)-H(24J)	0.9800	C(21U)-H(21E)	0.9800
C(24S)-H(24K)	0.9800	C(21U)-H(21F)	0.9800
C(24S)-H(24L)	0.9800	C(21U)-H(21G)	0.9800
C(11T)-C(12T)	1.515(5)	C(22U)-C(23U)	1.448(11)
C(11T)-H(11E)	0.9800	C(22U)-H(22J)	0.9900
C(11T)-H(11F)	0.9800	C(22U)-H(22K)	0.9900
C(11T)-H(11G)	0.9800	C(23U)-C(24U)	1.457(12)
C(12T)-C(13T)	1.474(6)	C(23U)-H(23J)	0.9900
C(12T)-H(12G)	0.9900	C(23U)-H(23K)	0.9900
C(12T)-H(12H)	0.9900	C(24U)-C(25U)	1.444(13)
C(13T)-C(14T)	1.416(9)	C(24U)-H(24M)	0.9900
C(13T)-H(13E)	0.9900	C(24U)-H(24N)	0.9900
C(13T)-H(13F)	0.9900	C(25U)-H(25A)	0.9800
C(14T)-C(15T)	1.503(10)	C(25U)-H(25B)	0.9800
C(14T)-H(14G)	0.9900	C(25U)-H(25C)	0.9800
C(14T)-H(14H)	0.9900		
C(15T)-H(15A)	0.9800	O(1)-Zr(1)-O(2)	155.34(5)
C(15T)-H(15B)	0.9800	O(1)-Zr(1)-C(51)	99.53(7)
C(15T)-H(15C)	0.9800	O(2)-Zr(1)-C(51)	99.12(6)
C(11U)-C(12U)	1.518(8)	O(1)-Zr(1)-C(1)	78.28(5)
C(11U)-H(11H)	0.9800	O(2)-Zr(1)-C(1)	78.88(5)
C(11U)-H(11I)	0.9800	C(51)-Zr(1)-C(1)	117.41(7)
C(11U)-H(11J)	0.9800	O(1)-Zr(1)-O(2B)	101.3(2)
C(12U)-C(13U)	1.450(11)	O(2)-Zr(1)-O(2B)	94.0(3)
C(12U)-H(12I)	0.9900	C(51)-Zr(1)-O(2B)	91.9(3)
C(12U)-H(12J)	0.9900	C(1)-Zr(1)-O(2B)	150.5(3)
C(13U)-C(14U)	1.346(9)	O(1)-Zr(1)-O(2E)	93.78(9)
C(13U)-H(13G)	0.9900	O(2)-Zr(1)-O(2E)	103.93(9)
C(13U)-H(13H)	0.9900	C(51)-Zr(1)-O(2E)	84.55(9)
C(14U)-C(15U)	1.485(12)	C(1)-Zr(1)-O(2E)	157.44(9)
C(14U)-H(14I)	0.9900	O(1)-Zr(1)-O(1E)	82.82(5)

O(2)-Zr(1)-O(1E)	84.71(5)	C(17)-C(18)-H(18C)	109.5
C(51)-Zr(1)-O(1E)	161.18(6)	H(18A)-C(18)-H(18C)	109.5
C(1)-Zr(1)-O(1E)	81.39(5)	H(18B)-C(18)-H(18C)	109.5
O(2B)-Zr(1)-O(1E)	69.4(3)	C(17)-C(19)-H(19A)	109.5
O(2E)-Zr(1)-O(1E)	76.66(8)	C(17)-C(19)-H(19B)	109.5
O(1)-Zr(1)-C(52)	93.06(6)	H(19A)-C(19)-H(19B)	109.5
O(2)-Zr(1)-C(52)	93.36(6)	C(17)-C(19)-H(19C)	109.5
C(51)-Zr(1)-C(52)	34.18(7)	H(19A)-C(19)-H(19C)	109.5
C(1)-Zr(1)-C(52)	83.23(6)	H(19B)-C(19)-H(19C)	109.5
O(2B)-Zr(1)-C(52)	126.1(3)	C(17)-C(20)-H(20A)	109.5
O(2E)-Zr(1)-C(52)	118.55(9)	C(17)-C(20)-H(20B)	109.5
O(1E)-Zr(1)-C(52)	164.58(6)	H(20A)-C(20)-H(20B)	109.5
N(2)-C(1)-N(1)	106.62(14)	C(17)-C(20)-H(20C)	109.5
N(2)-C(1)-Zr(1)	122.70(11)	H(20A)-C(20)-H(20C)	109.5
N(1)-C(1)-Zr(1)	124.14(11)	H(20B)-C(20)-H(20C)	109.5
C(1)-N(1)-C(2)	110.29(14)	C(13)-C(14)-C(15)	123.81(16)
C(1)-N(1)-C(31)	123.76(14)	C(13)-C(14)-H(14)	118.1
C(2)-N(1)-C(31)	125.66(14)	C(15)-C(14)-H(14)	118.1
C(12)-C(11)-C(16)	121.63(15)	C(16)-C(15)-C(14)	117.46(16)
C(12)-C(11)-N(2)	120.49(14)	C(16)-C(15)-C(21)	122.12(16)
C(16)-C(11)-N(2)	117.62(15)	C(14)-C(15)-C(21)	120.37(16)
O(2)-C(12)-C(11)	119.36(15)	C(24)-C(21)-C(22)	108.70(18)
O(2)-C(12)-C(13)	122.02(15)	C(24)-C(21)-C(15)	111.87(15)
C(11)-C(12)-C(13)	118.50(15)	C(22)-C(21)-C(15)	110.10(16)
C(14)-C(13)-C(12)	117.68(16)	C(24)-C(21)-C(23)	108.41(18)
C(14)-C(13)-C(17)	121.02(15)	C(22)-C(21)-C(23)	109.15(17)
C(12)-C(13)-C(17)	121.25(15)	C(15)-C(21)-C(23)	108.56(17)
C(13)-C(17)-C(20)	110.08(15)	C(21)-C(22)-H(22A)	109.5
C(13)-C(17)-C(18)	112.28(15)	C(21)-C(22)-H(22B)	109.5
C(20)-C(17)-C(18)	106.91(16)	H(22A)-C(22)-H(22B)	109.5
C(13)-C(17)-C(19)	109.36(15)	C(21)-C(22)-H(22C)	109.5
C(20)-C(17)-C(19)	111.40(17)	H(22A)-C(22)-H(22C)	109.5
C(18)-C(17)-C(19)	106.76(16)	H(22B)-C(22)-H(22C)	109.5
C(17)-C(18)-H(18A)	109.5	C(21)-C(23)-H(23A)	109.5
C(17)-C(18)-H(18B)	109.5	C(21)-C(23)-H(23B)	109.5
H(18A)-C(18)-H(18B)	109.5	H(23A)-C(23)-H(23B)	109.5

C(21)-C(23)-H(23C)	109.5	C(32)-C(31)-N(1)	120.31(15)
H(23A)-C(23)-H(23C)	109.5	O(1)-C(32)-C(31)	119.63(15)
H(23B)-C(23)-H(23C)	109.5	O(1)-C(32)-C(33)	121.23(15)
C(21)-C(24)-H(24A)	109.5	C(31)-C(32)-C(33)	119.12(15)
C(21)-C(24)-H(24B)	109.5	C(34)-C(33)-C(32)	117.68(16)
H(24A)-C(24)-H(24B)	109.5	C(34)-C(33)-C(37)	120.97(15)
C(21)-C(24)-H(24C)	109.5	C(32)-C(33)-C(37)	121.33(16)
H(24A)-C(24)-H(24C)	109.5	C(39)-C(37)-C(38)	110.25(17)
H(24B)-C(24)-H(24C)	109.5	C(39)-C(37)-C(33)	108.41(16)
C(15)-C(16)-C(11)	120.44(16)	C(38)-C(37)-C(33)	112.00(15)
C(15)-C(16)-H(16)	119.8	C(39)-C(37)-C(40)	107.36(16)
C(11)-C(16)-H(16)	119.8	C(38)-C(37)-C(40)	106.56(16)
C(32)-O(1)-Zr(1)	141.93(11)	C(33)-C(37)-C(40)	112.17(15)
C(3)-C(2)-C(7)	120.98(16)	C(37)-C(38)-H(38A)	109.5
C(3)-C(2)-N(1)	132.82(15)	C(37)-C(38)-H(38B)	109.5
C(7)-C(2)-N(1)	105.97(14)	H(38A)-C(38)-H(38B)	109.5
C(4)-C(3)-C(2)	117.01(16)	C(37)-C(38)-H(38C)	109.5
C(4)-C(3)-H(3)	121.5	H(38A)-C(38)-H(38C)	109.5
C(2)-C(3)-H(3)	121.5	H(38B)-C(38)-H(38C)	109.5
C(3)-C(4)-C(5)	121.73(17)	C(37)-C(39)-H(39A)	109.5
C(3)-C(4)-H(4)	119.1	C(37)-C(39)-H(39B)	109.5
C(5)-C(4)-H(4)	119.1	H(39A)-C(39)-H(39B)	109.5
C(6)-C(5)-C(4)	121.47(17)	C(37)-C(39)-H(39C)	109.5
C(6)-C(5)-H(5)	119.3	H(39A)-C(39)-H(39C)	109.5
C(4)-C(5)-H(5)	119.3	H(39B)-C(39)-H(39C)	109.5
C(5)-C(6)-C(7)	116.88(16)	C(37)-C(40)-H(40A)	109.5
C(5)-C(6)-H(6)	121.6	C(37)-C(40)-H(40B)	109.5
C(7)-C(6)-H(6)	121.6	H(40A)-C(40)-H(40B)	109.5
C(6)-C(7)-C(2)	121.93(16)	C(37)-C(40)-H(40C)	109.5
C(6)-C(7)-N(2)	131.30(16)	H(40A)-C(40)-H(40C)	109.5
C(2)-C(7)-N(2)	106.52(14)	H(40B)-C(40)-H(40C)	109.5
C(1)-N(2)-C(7)	110.45(14)	C(33)-C(34)-C(35)	123.71(16)
C(1)-N(2)-C(11)	124.51(14)	C(33)-C(34)-H(34)	118.1
C(7)-N(2)-C(11)	124.67(14)	C(35)-C(34)-H(34)	118.1
C(36)-C(31)-C(32)	121.08(15)	C(36)-C(35)-C(34)	117.51(16)
C(36)-C(31)-N(1)	118.51(15)	C(36)-C(35)-C(41)	119.61(16)

C(34)-C(35)-C(41)	122.86(16)	C(53)-C(52)-C(51)	121.82(18)
C(35)-C(41)-C(44)	112.12(16)	C(57)-C(52)-C(51)	121.25(18)
C(35)-C(41)-C(42)	109.22(17)	C(53)-C(52)-Zr(1)	101.53(12)
C(44)-C(41)-C(42)	108.31(18)	C(57)-C(52)-Zr(1)	101.32(12)
C(35)-C(41)-C(43)	109.46(16)	C(51)-C(52)-Zr(1)	61.23(10)
C(44)-C(41)-C(43)	108.20(18)	C(54)-C(53)-C(52)	121.69(19)
C(42)-C(41)-C(43)	109.50(19)	C(54)-C(53)-H(53)	119.2
C(41)-C(42)-H(42A)	109.5	C(52)-C(53)-H(53)	119.2
C(41)-C(42)-H(42B)	109.5	C(53)-C(54)-C(55)	120.6(2)
H(42A)-C(42)-H(42B)	109.5	C(53)-C(54)-H(54)	119.7
C(41)-C(42)-H(42C)	109.5	C(55)-C(54)-H(54)	119.7
H(42A)-C(42)-H(42C)	109.5	C(56)-C(55)-C(54)	119.0(2)
H(42B)-C(42)-H(42C)	109.5	C(56)-C(55)-H(55)	120.5
C(41)-C(43)-H(43A)	109.5	C(54)-C(55)-H(55)	120.5
C(41)-C(43)-H(43B)	109.5	C(57)-C(56)-C(55)	120.3(2)
H(43A)-C(43)-H(43B)	109.5	C(57)-C(56)-H(56)	119.8
C(41)-C(43)-H(43C)	109.5	C(55)-C(56)-H(56)	119.8
H(43A)-C(43)-H(43C)	109.5	C(56)-C(57)-C(52)	121.84(19)
H(43B)-C(43)-H(43C)	109.5	C(56)-C(57)-H(57)	119.1
C(41)-C(44)-H(44A)	109.5	C(52)-C(57)-H(57)	119.1
C(41)-C(44)-H(44B)	109.5	C(11E)-O(1E)-C(13E)	114.05(16)
H(44A)-C(44)-H(44B)	109.5	C(11E)-O(1E)-Zr(1)	120.30(12)
C(41)-C(44)-H(44C)	109.5	C(13E)-O(1E)-Zr(1)	123.70(11)
H(44A)-C(44)-H(44C)	109.5	O(1E)-C(11E)-C(12E)	113.07(19)
H(44B)-C(44)-H(44C)	109.5	O(1E)-C(11E)-H(11A)	109.0
C(31)-C(36)-C(35)	120.76(16)	C(12E)-C(11E)-H(11A)	109.0
C(31)-C(36)-H(36)	119.6	O(1E)-C(11E)-H(11B)	109.0
C(35)-C(36)-H(36)	119.6	C(12E)-C(11E)-H(11B)	109.0
C(12)-O(2)-Zr(1)	140.62(11)	H(11A)-C(11E)-H(11B)	107.8
C(52)-C(51)-Zr(1)	84.59(11)	C(11E)-C(12E)-H(12A)	109.5
C(52)-C(51)-H(51A)	114.5	C(11E)-C(12E)-H(12B)	109.5
Zr(1)-C(51)-H(51A)	114.5	H(12A)-C(12E)-H(12B)	109.5
C(52)-C(51)-H(51B)	114.5	C(11E)-C(12E)-H(12C)	109.5
Zr(1)-C(51)-H(51B)	114.5	H(12A)-C(12E)-H(12C)	109.5
H(51A)-C(51)-H(51B)	111.7	H(12B)-C(12E)-H(12C)	109.5
C(53)-C(52)-C(57)	116.45(19)	O(1E)-C(13E)-C(14E)	113.63(18)

O(1E)-C(13E)-H(13A)	108.8	C(23E)-C(24E)-H(24F)	109.5
C(14E)-C(13E)-H(13A)	108.8	H(24D)-C(24E)-H(24F)	109.5
O(1E)-C(13E)-H(13B)	108.8	H(24E)-C(24E)-H(24F)	109.5
C(14E)-C(13E)-H(13B)	108.8	C(23B)-O(2B)-C(21E)	123.4(9)
H(13A)-C(13E)-H(13B)	107.7	C(23B)-O(2B)-Zr(1)	116.3(7)
C(13E)-C(14E)-H(14A)	109.5	C(21E)-O(2B)-Zr(1)	118.2(5)
C(13E)-C(14E)-H(14B)	109.5	O(2B)-C(23B)-C(24B)	113.0(11)
H(14A)-C(14E)-H(14B)	109.5	O(2B)-C(23B)-H(23F)	109.0
C(13E)-C(14E)-H(14C)	109.5	C(24B)-C(23B)-H(23F)	109.0
H(14A)-C(14E)-H(14C)	109.5	O(2B)-C(23B)-H(23G)	109.0
H(14B)-C(14E)-H(14C)	109.5	C(24B)-C(23B)-H(23G)	109.0
O(2E)-C(21E)-C(22E)	115.4(2)	H(23F)-C(23B)-H(23G)	107.8
C(22E)-C(21E)-O(2B)	101.3(5)	C(23B)-C(24B)-H(24G)	109.5
O(2E)-C(21E)-H(21A)	108.4	C(23B)-C(24B)-H(24H)	109.5
C(22E)-C(21E)-H(21A)	108.4	H(24G)-C(24B)-H(24H)	109.5
O(2E)-C(21E)-H(21B)	108.4	C(23B)-C(24B)-H(24I)	109.5
C(22E)-C(21E)-H(21B)	108.4	H(24G)-C(24B)-H(24I)	109.5
H(21A)-C(21E)-H(21B)	107.5	H(24H)-C(24B)-H(24I)	109.5
C(21E)-C(22E)-H(22D)	109.5	C(81)-B(1)-C(91)	101.81(14)
C(21E)-C(22E)-H(22E)	109.5	C(81)-B(1)-C(61)	112.70(14)
H(22D)-C(22E)-H(22E)	109.5	C(91)-B(1)-C(61)	114.54(14)
C(21E)-C(22E)-H(22F)	109.5	C(81)-B(1)-C(71)	113.46(14)
H(22D)-C(22E)-H(22F)	109.5	C(91)-B(1)-C(71)	113.06(14)
H(22E)-C(22E)-H(22F)	109.5	C(61)-B(1)-C(71)	101.78(14)
C(21E)-O(2E)-C(23E)	109.5(3)	C(62)-C(61)-C(66)	113.30(17)
C(21E)-O(2E)-Zr(1)	124.5(2)	C(62)-C(61)-B(1)	127.30(16)
C(23E)-O(2E)-Zr(1)	124.4(2)	C(66)-C(61)-B(1)	119.11(16)
O(2E)-C(23E)-C(24E)	110.9(3)	F(1)-C(62)-C(61)	121.16(16)
O(2E)-C(23E)-H(23D)	109.5	F(1)-C(62)-C(63)	114.57(17)
C(24E)-C(23E)-H(23D)	109.5	C(61)-C(62)-C(63)	124.26(18)
O(2E)-C(23E)-H(23E)	109.5	F(2)-C(63)-C(64)	120.45(18)
C(24E)-C(23E)-H(23E)	109.5	F(2)-C(63)-C(62)	120.09(18)
H(23D)-C(23E)-H(23E)	108.1	C(64)-C(63)-C(62)	119.47(19)
C(23E)-C(24E)-H(24D)	109.5	F(3)-C(64)-C(63)	120.1(2)
C(23E)-C(24E)-H(24E)	109.5	F(3)-C(64)-C(65)	120.7(2)
H(24D)-C(24E)-H(24E)	109.5	C(63)-C(64)-C(65)	119.17(18)

F(4)-C(65)-C(64)	119.77(19)	F(14)-C(85)-C(84)	120.02(18)
F(4)-C(65)-C(66)	120.8(2)	F(14)-C(85)-C(86)	120.50(19)
C(64)-C(65)-C(66)	119.46(19)	C(84)-C(85)-C(86)	119.48(19)
F(5)-C(66)-C(65)	116.16(17)	F(15)-C(86)-C(85)	115.11(17)
F(5)-C(66)-C(61)	119.51(17)	F(15)-C(86)-C(81)	121.13(16)
C(65)-C(66)-C(61)	124.33(19)	C(85)-C(86)-C(81)	123.75(18)
C(76)-C(71)-C(72)	113.01(17)	C(92)-C(91)-C(96)	113.24(16)
C(76)-C(71)-B(1)	127.63(16)	C(92)-C(91)-B(1)	126.90(16)
C(72)-C(71)-B(1)	119.14(16)	C(96)-C(91)-B(1)	119.30(15)
F(6)-C(72)-C(73)	116.25(17)	F(16)-C(92)-C(93)	114.55(16)
F(6)-C(72)-C(71)	119.26(17)	F(16)-C(92)-C(91)	121.33(16)
C(73)-C(72)-C(71)	124.49(18)	C(93)-C(92)-C(91)	124.13(18)
F(7)-C(73)-C(74)	119.63(19)	F(17)-C(93)-C(94)	119.77(17)
F(7)-C(73)-C(72)	120.64(18)	F(17)-C(93)-C(92)	120.50(18)
C(74)-C(73)-C(72)	119.73(19)	C(94)-C(93)-C(92)	119.73(17)
F(8)-C(74)-C(75)	120.66(19)	F(18)-C(94)-C(93)	120.83(18)
F(8)-C(74)-C(73)	120.70(19)	F(18)-C(94)-C(95)	120.15(19)
C(75)-C(74)-C(73)	118.64(19)	C(93)-C(94)-C(95)	119.02(17)
F(9)-C(75)-C(74)	119.49(19)	F(19)-C(95)-C(94)	119.67(17)
F(9)-C(75)-C(76)	120.71(18)	F(19)-C(95)-C(96)	121.14(17)
C(74)-C(75)-C(76)	119.80(19)	C(94)-C(95)-C(96)	119.19(18)
F(10)-C(76)-C(75)	114.64(17)	F(20)-C(96)-C(95)	115.83(16)
F(10)-C(76)-C(71)	121.04(17)	F(20)-C(96)-C(91)	119.49(16)
C(75)-C(76)-C(71)	124.31(18)	C(95)-C(96)-C(91)	124.68(17)
C(86)-C(81)-C(82)	113.64(17)	C(11S)-O(1S)-C(13S)	110.9(3)
C(86)-C(81)-B(1)	127.22(16)	O(1S)-C(11S)-C(12S)	109.2(3)
C(82)-C(81)-B(1)	118.82(16)	O(1S)-C(11S)-H(11C)	109.8
F(11)-C(82)-C(83)	116.31(17)	C(12S)-C(11S)-H(11C)	109.8
F(11)-C(82)-C(81)	119.40(16)	O(1S)-C(11S)-H(11D)	109.8
C(83)-C(82)-C(81)	124.29(18)	C(12S)-C(11S)-H(11D)	109.8
F(12)-C(83)-C(84)	119.66(18)	H(11C)-C(11S)-H(11D)	108.3
F(12)-C(83)-C(82)	120.9(2)	C(11S)-C(12S)-H(12D)	109.5
C(84)-C(83)-C(82)	119.42(19)	C(11S)-C(12S)-H(12E)	109.5
F(13)-C(84)-C(83)	120.2(2)	H(12D)-C(12S)-H(12E)	109.5
F(13)-C(84)-C(85)	120.4(2)	C(11S)-C(12S)-H(12F)	109.5
C(83)-C(84)-C(85)	119.37(18)	H(12D)-C(12S)-H(12F)	109.5

H(12E)-C(12S)-H(12F)	109.5	H(24J)-C(24S)-H(24L)	109.5
O(1S)-C(13S)-C(14S)	107.7(3)	H(24K)-C(24S)-H(24L)	109.5
O(1S)-C(13S)-H(13C)	110.2	C(12T)-C(11T)-H(11E)	109.5
C(14S)-C(13S)-H(13C)	110.2	C(12T)-C(11T)-H(11F)	109.5
O(1S)-C(13S)-H(13D)	110.2	H(11E)-C(11T)-H(11F)	109.5
C(14S)-C(13S)-H(13D)	110.2	C(12T)-C(11T)-H(11G)	109.5
H(13C)-C(13S)-H(13D)	108.5	H(11E)-C(11T)-H(11G)	109.5
C(13S)-C(14S)-H(14D)	109.5	H(11F)-C(11T)-H(11G)	109.5
C(13S)-C(14S)-H(14E)	109.5	C(13T)-C(12T)-C(11T)	109.6(4)
H(14D)-C(14S)-H(14E)	109.5	C(13T)-C(12T)-H(12G)	109.8
C(13S)-C(14S)-H(14F)	109.5	C(11T)-C(12T)-H(12G)	109.8
H(14D)-C(14S)-H(14F)	109.5	C(13T)-C(12T)-H(12H)	109.8
H(14E)-C(14S)-H(14F)	109.5	C(11T)-C(12T)-H(12H)	109.8
C(23S)-O(2S)-C(21S)	116.1(4)	H(12G)-C(12T)-H(12H)	108.2
C(22S)-C(21S)-O(2S)	115.4(6)	C(14T)-C(13T)-C(12T)	124.3(6)
C(22S)-C(21S)-H(21C)	108.4	C(14T)-C(13T)-H(13E)	106.3
O(2S)-C(21S)-H(21C)	108.4	C(12T)-C(13T)-H(13E)	106.3
C(22S)-C(21S)-H(21D)	108.4	C(14T)-C(13T)-H(13F)	106.3
O(2S)-C(21S)-H(21D)	108.4	C(12T)-C(13T)-H(13F)	106.3
H(21C)-C(21S)-H(21D)	107.5	H(13E)-C(13T)-H(13F)	106.4
C(21S)-C(22S)-H(22G)	109.5	C(13T)-C(14T)-C(15T)	112.3(9)
C(21S)-C(22S)-H(22H)	109.5	C(13T)-C(14T)-H(14G)	109.1
H(22G)-C(22S)-H(22H)	109.5	C(15T)-C(14T)-H(14G)	109.1
C(21S)-C(22S)-H(22I)	109.5	C(13T)-C(14T)-H(14H)	109.1
H(22G)-C(22S)-H(22I)	109.5	C(15T)-C(14T)-H(14H)	109.1
H(22H)-C(22S)-H(22I)	109.5	H(14G)-C(14T)-H(14H)	107.9
C(24S)-C(23S)-O(2S)	114.7(5)	C(14T)-C(15T)-H(15A)	109.5
C(24S)-C(23S)-H(23H)	108.6	C(14T)-C(15T)-H(15B)	109.5
O(2S)-C(23S)-H(23H)	108.6	H(15A)-C(15T)-H(15B)	109.5
C(24S)-C(23S)-H(23I)	108.6	C(14T)-C(15T)-H(15C)	109.5
O(2S)-C(23S)-H(23I)	108.6	H(15A)-C(15T)-H(15C)	109.5
H(23H)-C(23S)-H(23I)	107.6	H(15B)-C(15T)-H(15C)	109.5
C(23S)-C(24S)-H(24J)	109.5	C(12U)-C(11U)-H(11H)	109.5
C(23S)-C(24S)-H(24K)	109.5	C(12U)-C(11U)-H(11I)	109.5
H(24J)-C(24S)-H(24K)	109.5	H(11H)-C(11U)-H(11I)	109.5
C(23S)-C(24S)-H(24L)	109.5	C(12U)-C(11U)-H(11J)	109.5

H(11H)-C(11U)-H(11J)	109.5
H(11I)-C(11U)-H(11J)	109.5
C(13U)-C(12U)-C(11U)	107.0(8)
C(13U)-C(12U)-H(12I)	110.3
C(11U)-C(12U)-H(12I)	110.3
C(13U)-C(12U)-H(12J)	110.3
C(11U)-C(12U)-H(12J)	110.3
H(12I)-C(12U)-H(12J)	108.6
C(14U)-C(13U)-C(12U)	129.0(11)
C(14U)-C(13U)-H(13G)	105.0
C(12U)-C(13U)-H(13G)	105.0
C(14U)-C(13U)-H(13H)	105.0
C(12U)-C(13U)-H(13H)	105.0
H(13G)-C(13U)-H(13H)	105.9
C(13U)-C(14U)-C(15U)	120.6(11)
C(13U)-C(14U)-H(14I)	107.2
C(15U)-C(14U)-H(14I)	107.2
C(13U)-C(14U)-H(14J)	107.2
C(15U)-C(14U)-H(14J)	107.2
H(14I)-C(14U)-H(14J)	106.8
C(14U)-C(15U)-H(15D)	109.5
C(14U)-C(15U)-H(15E)	109.5
H(15D)-C(15U)-H(15E)	109.5
C(14U)-C(15U)-H(15F)	109.5
H(15D)-C(15U)-H(15F)	109.5
H(15E)-C(15U)-H(15F)	109.5
C(22U)-C(21U)-H(21E)	109.5
C(22U)-C(21U)-H(21F)	109.5
H(21E)-C(21U)-H(21F)	109.5
C(22U)-C(21U)-H(21G)	109.5
H(21E)-C(21U)-H(21G)	109.5
H(21F)-C(21U)-H(21G)	109.5
C(23U)-C(22U)-C(21U)	113.2(12)
C(23U)-C(22U)-H(22J)	108.9
C(21U)-C(22U)-H(22J)	108.9
C(23U)-C(22U)-H(22K)	108.9
C(21U)-C(22U)-H(22K)	108.9
H(22J)-C(22U)-H(22K)	107.7
C(22U)-C(23U)-C(24U)	112.0(10)
C(22U)-C(23U)-H(23J)	109.2
C(24U)-C(23U)-H(23J)	109.2
C(22U)-C(23U)-H(23K)	109.2
C(24U)-C(23U)-H(23K)	109.2
H(23J)-C(23U)-H(23K)	107.9
C(25U)-C(24U)-C(23U)	112.5(13)
C(25U)-C(24U)-H(24M)	109.1
C(23U)-C(24U)-H(24M)	109.1
C(25U)-C(24U)-H(24N)	109.1
C(23U)-C(24U)-H(24N)	109.1
H(24M)-C(24U)-H(24N)	107.8
C(24U)-C(25U)-H(25A)	109.5
C(24U)-C(25U)-H(25B)	109.5
H(25A)-C(25U)-H(25B)	109.5
C(24U)-C(25U)-H(25C)	109.5
H(25A)-C(25U)-H(25C)	109.5
H(25B)-C(25U)-H(25C)	109.5

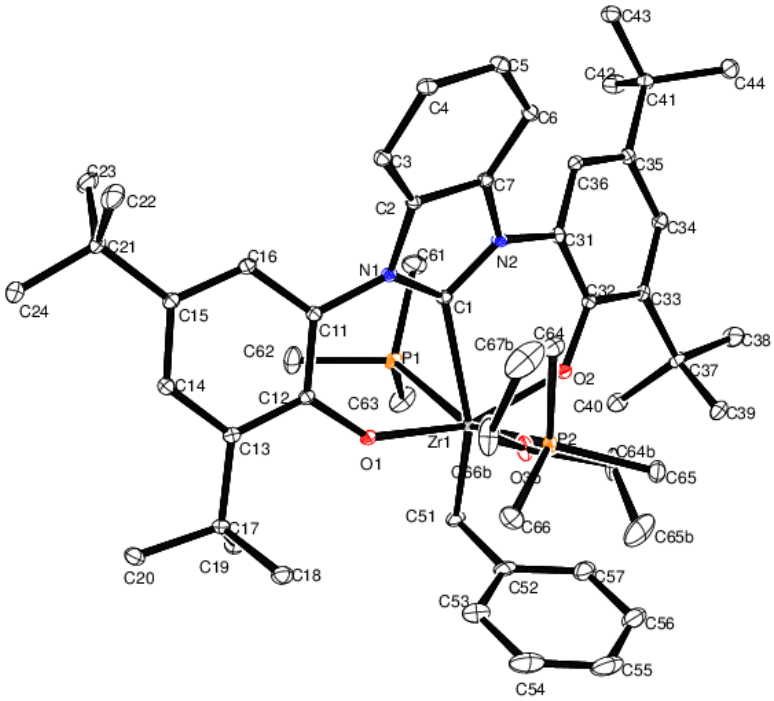


Figure S46: Molecular structure of complexes 3/4 (CCDC 1402121)**.** The counter anion ($B(C_6F_5)_4$) and the hydrogens were omitted for clarity.

Low-temperature diffraction data (ϕ-and ω-scans) were collected on a Bruker Kappa diffractometer coupled to a Apex II CCD detector with graphite monochromated Mo K_α radiation (λ = 0.71073 Å) for the structure of compounds **3**/**4**. The structure was solved by direct methods using SHELXS[i] and refined against F^2 on all data by full-matrix least squares with SHELXL-2013[ii] using established refinement techniques.[iii] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups).

Compounds **3**/**4** crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit along with one molecule of ether. One of the two PMe_3 ligands was modeled as a two component disorder with a partially occupied ether. The occupancy of the two components refined to 0.720(3):0.280(3) for PMe_3 and ether, respectively. This disorder was refined with the help of similarity and rigid bond restraints for anisotropic displacement parameters.

Table 5: Crystal data and structure refinement for 3/4.

Empirical formula	C76.28 H79.28 B F20 N2 O3.28 P1.72 Zr	
Formula weight	1611.83	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 11.8600(7) Å	α= 90°.
	b = 38.051(2) Å	β= 105.328(3)°.
	c = 17.0394(10) Å	γ = 90°.
Volume	7416.0(8) $Å^3$	
Z	4	
Density (calculated)	1.444 Mg/m^3	
Absorption coefficient	0.285 mm^{-1}	
F(000)	3312	
Crystal size	0.300 x 0.250 x 0.200 mm^3	
Theta range for data collection	1.070 to 30.646°.	
Index ranges	-16<=h<=16, -54<=k<=54, -24<=l<=24	
Reflections collected	193632	
Independent reflections	22826 [R(int) = 0.0548]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.6951	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	22826 / 110 / 1014	
Goodness-of-fit on F^2	1.165	
Final R indices [I>2sigma(I)]	R1 = 0.0443, wR2 = 0.0914	
R indices (all data)	R1 = 0.0553, wR2 = 0.0962	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.735 and -0.632 $e.Å^{-3}$	

Table 6: Bond lengths [Å] and angles [°] for 3/4.

P(1)-C(62)	1.816(2)	C(64B)-C(65B)	1.500(11)
P(1)-C(61)	1.817(2)	C(64B)-H(64D)	0.9900
P(1)-C(63)	1.821(2)	C(64B)-H(64E)	0.9900
P(1)-Zr(1)	2.7772(5)	C(65B)-H(65D)	0.9800
C(61)-H(61A)	0.9800	C(65B)-H(65E)	0.9800
C(61)-H(61B)	0.9800	C(65B)-H(65F)	0.9800
C(61)-H(61C)	0.9800	C(66B)-C(67B)	1.525(14)
C(62)-H(62A)	0.9800	C(66B)-H(66D)	0.9900
C(62)-H(62B)	0.9800	C(66B)-H(66E)	0.9900
C(62)-H(62C)	0.9800	C(67B)-H(67A)	0.9800
C(63)-H(63A)	0.9800	C(67B)-H(67B)	0.9800
C(63)-H(63B)	0.9800	C(67B)-H(67C)	0.9800
C(63)-H(63C)	0.9800	C(1)-N(1)	1.359(2)
Zr(1)-O(1)	1.9958(12)	C(1)-N(2)	1.362(2)
Zr(1)-O(2)	1.9986(12)	N(1)-C(2)	1.408(2)
Zr(1)-O(3B)	2.215(7)	N(1)-C(11)	1.429(2)
Zr(1)-C(51)	2.2907(17)	C(11)-C(16)	1.387(2)
Zr(1)-C(1)	2.3235(16)	C(11)-C(12)	1.407(2)
Zr(1)-C(52)	2.6769(17)	C(12)-O(1)	1.3478(19)
Zr(1)-P(2)	2.8269(10)	C(12)-C(13)	1.413(2)
P(2)-C(66)	1.812(3)	C(13)-C(14)	1.399(2)
P(2)-C(65)	1.819(3)	C(13)-C(17)	1.539(2)
P(2)-C(64)	1.826(3)	C(17)-C(20)	1.533(2)
C(64)-H(64A)	0.9800	C(17)-C(19)	1.535(2)
C(64)-H(64B)	0.9800	C(17)-C(18)	1.541(2)
C(64)-H(64C)	0.9800	C(18)-H(18A)	0.9800
C(65)-H(65A)	0.9800	C(18)-H(18B)	0.9800
C(65)-H(65B)	0.9800	C(18)-H(18C)	0.9800
C(65)-H(65C)	0.9800	C(19)-H(19A)	0.9800
C(66)-H(66A)	0.9800	C(19)-H(19B)	0.9800
C(66)-H(66B)	0.9800	C(19)-H(19C)	0.9800
C(66)-H(66C)	0.9800	C(20)-H(20A)	0.9800
O(3B)-C(64B)	1.470(9)	C(20)-H(20B)	0.9800
O(3B)-C(66B)	1.473(9)	C(20)-H(20C)	0.9800

C(14)-C(15)	1.400(2)	C(37)-C(38)	1.536(3)
C(14)-H(14)	0.9500	C(37)-C(40)	1.538(3)
C(15)-C(16)	1.386(2)	C(38)-H(38A)	0.9800
C(15)-C(21)	1.536(2)	C(38)-H(38B)	0.9800
C(21)-C(24)	1.525(3)	C(38)-H(38C)	0.9800
C(21)-C(23)	1.532(3)	C(39)-H(39A)	0.9800
C(21)-C(22)	1.538(3)	C(39)-H(39B)	0.9800
C(22)-H(22A)	0.9800	C(39)-H(39C)	0.9800
C(22)-H(22B)	0.9800	C(40)-H(40A)	0.9800
C(22)-H(22C)	0.9800	C(40)-H(40B)	0.9800
C(23)-H(23A)	0.9800	C(40)-H(40C)	0.9800
C(23)-H(23B)	0.9800	C(34)-C(35)	1.398(2)
C(23)-H(23C)	0.9800	C(34)-H(34)	0.9500
C(24)-H(24A)	0.9800	C(35)-C(36)	1.384(2)
C(24)-H(24B)	0.9800	C(35)-C(41)	1.531(2)
C(24)-H(24C)	0.9800	C(41)-C(43)	1.532(2)
C(16)-H(16)	0.9500	C(41)-C(42)	1.533(2)
C(2)-C(3)	1.393(2)	C(41)-C(44)	1.537(3)
C(2)-C(7)	1.394(2)	C(42)-H(42A)	0.9800
C(3)-C(4)	1.382(2)	C(42)-H(42B)	0.9800
C(3)-H(3)	0.9500	C(42)-H(42C)	0.9800
C(4)-C(5)	1.401(3)	C(43)-H(43A)	0.9800
C(4)-H(4)	0.9500	C(43)-H(43B)	0.9800
C(5)-C(6)	1.381(2)	C(43)-H(43C)	0.9800
C(5)-H(5)	0.9500	C(44)-H(44A)	0.9800
C(6)-C(7)	1.395(2)	C(44)-H(44B)	0.9800
C(6)-H(6)	0.9500	C(44)-H(44C)	0.9800
C(7)-N(2)	1.404(2)	C(36)-H(36)	0.9500
N(2)-C(31)	1.432(2)	C(51)-C(52)	1.464(3)
C(31)-C(36)	1.393(2)	C(51)-H(51A)	0.9900
C(31)-C(32)	1.405(2)	C(51)-H(51B)	0.9900
C(32)-O(2)	1.353(2)	C(52)-C(53)	1.404(3)
C(32)-C(33)	1.416(2)	C(52)-C(57)	1.412(3)
C(33)-C(34)	1.393(2)	C(53)-C(54)	1.400(3)
C(33)-C(37)	1.534(2)	C(53)-H(53)	0.9500
C(37)-C(39)	1.536(2)	C(54)-C(55)	1.381(4)

C(54)-H(54)	0.9500	C(93)-F(12)	1.348(2)
C(55)-C(56)	1.381(4)	C(93)-C(94)	1.374(3)
C(55)-H(55)	0.9500	C(94)-F(13)	1.341(2)
C(56)-C(57)	1.382(3)	C(94)-C(95)	1.374(3)
C(56)-H(56)	0.9500	C(95)-F(14)	1.344(2)
C(57)-H(57)	0.9500	C(95)-C(96)	1.380(3)
B(1)-C(101)	1.647(3)	C(96)-F(15)	1.351(2)
B(1)-C(91)	1.654(3)	C(101)-C(102)	1.385(3)
B(1)-C(71)	1.658(3)	C(101)-C(106)	1.392(3)
B(1)-C(81)	1.662(3)	C(102)-F(16)	1.354(2)
C(71)-C(76)	1.384(3)	C(102)-C(103)	1.384(3)
C(71)-C(72)	1.392(2)	C(103)-F(17)	1.345(2)
C(72)-F(1)	1.345(2)	C(103)-C(104)	1.376(3)
C(72)-C(73)	1.384(3)	C(104)-F(18)	1.341(2)
C(73)-F(2)	1.344(2)	C(104)-C(105)	1.374(3)
C(73)-C(74)	1.374(3)	C(105)-F(19)	1.341(2)
C(74)-F(3)	1.341(2)	C(105)-C(106)	1.382(3)
C(74)-C(75)	1.374(3)	C(106)-F(20)	1.355(2)
C(75)-F(4)	1.337(3)	O(1S)-C(3S)	1.418(2)
C(75)-C(76)	1.392(3)	O(1S)-C(1S)	1.426(3)
C(76)-F(5)	1.350(2)	C(1S)-C(2S)	1.499(3)
C(81)-C(86)	1.390(2)	C(1S)-H(1S1)	0.9900
C(81)-C(82)	1.394(2)	C(1S)-H(1S2)	0.9900
C(82)-F(6)	1.353(2)	C(2S)-H(2S1)	0.9800
C(82)-C(83)	1.380(3)	C(2S)-H(2S2)	0.9800
C(83)-F(7)	1.345(2)	C(2S)-H(2S3)	0.9800
C(83)-C(84)	1.376(3)	C(3S)-C(4S)	1.501(3)
C(84)-F(8)	1.343(2)	C(3S)-H(3S1)	0.9900
C(84)-C(85)	1.373(3)	C(3S)-H(3S2)	0.9900
C(85)-F(9)	1.345(2)	C(4S)-H(4S1)	0.9800
C(85)-C(86)	1.387(2)	C(4S)-H(4S2)	0.9800
C(86)-F(10)	1.352(2)	C(4S)-H(4S3)	0.9800
C(91)-C(92)	1.386(2)		
C(91)-C(96)	1.393(2)	C(62)-P(1)-C(61)	103.12(11)
C(92)-F(11)	1.347(2)	C(62)-P(1)-C(63)	102.46(11)
C(92)-C(93)	1.385(2)	C(61)-P(1)-C(63)	100.70(11)

C(62)-P(1)-Zr(1)	111.33(7)	O(1)-Zr(1)-P(1)	90.95(4)
C(61)-P(1)-Zr(1)	116.02(7)	O(2)-Zr(1)-P(1)	88.52(4)
C(63)-P(1)-Zr(1)	120.94(7)	O(3B)-Zr(1)-P(1)	163.17(14)
P(1)-C(61)-H(61A)	109.5	C(51)-Zr(1)-P(1)	74.45(5)
P(1)-C(61)-H(61B)	109.5	C(1)-Zr(1)-P(1)	74.66(4)
H(61A)-C(61)-H(61B)	109.5	C(52)-Zr(1)-P(1)	107.32(4)
P(1)-C(61)-H(61C)	109.5	O(1)-Zr(1)-P(2)	86.03(4)
H(61A)-C(61)-H(61C)	109.5	O(2)-Zr(1)-P(2)	86.33(4)
H(61B)-C(61)-H(61C)	109.5	C(51)-Zr(1)-P(2)	124.87(5)
P(1)-C(62)-H(62A)	109.5	C(1)-Zr(1)-P(2)	86.05(4)
P(1)-C(62)-H(62B)	109.5	C(52)-Zr(1)-P(2)	91.91(4)
H(62A)-C(62)-H(62B)	109.5	P(1)-Zr(1)-P(2)	160.672(17)
P(1)-C(62)-H(62C)	109.5	C(66)-P(2)-C(65)	103.09(14)
H(62A)-C(62)-H(62C)	109.5	C(66)-P(2)-C(64)	101.18(14)
H(62B)-C(62)-H(62C)	109.5	C(65)-P(2)-C(64)	103.12(13)
P(1)-C(63)-H(63A)	109.5	C(66)-P(2)-Zr(1)	120.46(10)
P(1)-C(63)-H(63B)	109.5	C(65)-P(2)-Zr(1)	114.60(9)
H(63A)-C(63)-H(63B)	109.5	C(64)-P(2)-Zr(1)	112.21(10)
P(1)-C(63)-H(63C)	109.5	P(2)-C(64)-H(64A)	109.5
H(63A)-C(63)-H(63C)	109.5	P(2)-C(64)-H(64B)	109.5
H(63B)-C(63)-H(63C)	109.5	H(64A)-C(64)-H(64B)	109.5
O(1)-Zr(1)-O(2)	155.19(5)	P(2)-C(64)-H(64C)	109.5
O(1)-Zr(1)-O(3B)	82.75(14)	H(64A)-C(64)-H(64C)	109.5
O(2)-Zr(1)-O(3B)	90.72(14)	H(64B)-C(64)-H(64C)	109.5
O(1)-Zr(1)-C(51)	100.89(6)	P(2)-C(65)-H(65A)	109.5
O(2)-Zr(1)-C(51)	102.85(6)	P(2)-C(65)-H(65B)	109.5
O(3B)-Zr(1)-C(51)	122.01(15)	H(65A)-C(65)-H(65B)	109.5
O(1)-Zr(1)-C(1)	77.82(5)	P(2)-C(65)-H(65C)	109.5
O(2)-Zr(1)-C(1)	78.12(5)	H(65A)-C(65)-H(65C)	109.5
O(3B)-Zr(1)-C(1)	88.73(15)	H(65B)-C(65)-H(65C)	109.5
C(51)-Zr(1)-C(1)	149.05(6)	P(2)-C(66)-H(66A)	109.5
O(1)-Zr(1)-C(52)	104.20(6)	P(2)-C(66)-H(66B)	109.5
O(2)-Zr(1)-C(52)	99.62(6)	H(66A)-C(66)-H(66B)	109.5
O(3B)-Zr(1)-C(52)	89.38(15)	P(2)-C(66)-H(66C)	109.5
C(51)-Zr(1)-C(52)	33.13(6)	H(66A)-C(66)-H(66C)	109.5
C(1)-Zr(1)-C(52)	177.04(6)	H(66B)-C(66)-H(66C)	109.5

C(64B)-O(3B)-C(66B)	110.0(6)	O(1)-C(12)-C(11)	119.61(15)
C(64B)-O(3B)-Zr(1)	120.9(4)	O(1)-C(12)-C(13)	121.98(14)
C(66B)-O(3B)-Zr(1)	128.1(5)	C(11)-C(12)-C(13)	118.38(15)
O(3B)-C(64B)-C(65B)	115.3(7)	C(12)-O(1)-Zr(1)	144.21(11)
O(3B)-C(64B)-H(64D)	108.4	C(14)-C(13)-C(12)	117.99(15)
C(65B)-C(64B)-H(64D)	108.4	C(14)-C(13)-C(17)	120.98(15)
O(3B)-C(64B)-H(64E)	108.4	C(12)-C(13)-C(17)	121.03(14)
C(65B)-C(64B)-H(64E)	108.4	C(20)-C(17)-C(19)	107.30(14)
H(64D)-C(64B)-H(64E)	107.5	C(20)-C(17)-C(13)	111.99(14)
C(64B)-C(65B)-H(65D)	109.5	C(19)-C(17)-C(13)	110.29(14)
C(64B)-C(65B)-H(65E)	109.5	C(20)-C(17)-C(18)	107.36(14)
H(65D)-C(65B)-H(65E)	109.5	C(19)-C(17)-C(18)	109.86(14)
C(64B)-C(65B)-H(65F)	109.5	C(13)-C(17)-C(18)	109.96(14)
H(65D)-C(65B)-H(65F)	109.5	C(17)-C(18)-H(18A)	109.5
H(65E)-C(65B)-H(65F)	109.5	C(17)-C(18)-H(18B)	109.5
O(3B)-C(66B)-C(67B)	113.1(9)	H(18A)-C(18)-H(18B)	109.5
O(3B)-C(66B)-H(66D)	109.0	C(17)-C(18)-H(18C)	109.5
C(67B)-C(66B)-H(66D)	109.0	H(18A)-C(18)-H(18C)	109.5
O(3B)-C(66B)-H(66E)	109.0	H(18B)-C(18)-H(18C)	109.5
C(67B)-C(66B)-H(66E)	109.0	C(17)-C(19)-H(19A)	109.5
H(66D)-C(66B)-H(66E)	107.8	C(17)-C(19)-H(19B)	109.5
C(66B)-C(67B)-H(67A)	109.5	H(19A)-C(19)-H(19B)	109.5
C(66B)-C(67B)-H(67B)	109.5	C(17)-C(19)-H(19C)	109.5
H(67A)-C(67B)-H(67B)	109.5	H(19A)-C(19)-H(19C)	109.5
C(66B)-C(67B)-H(67C)	109.5	H(19B)-C(19)-H(19C)	109.5
H(67A)-C(67B)-H(67C)	109.5	C(17)-C(20)-H(20A)	109.5
H(67B)-C(67B)-H(67C)	109.5	C(17)-C(20)-H(20B)	109.5
N(1)-C(1)-N(2)	106.17(13)	H(20A)-C(20)-H(20B)	109.5
N(1)-C(1)-Zr(1)	123.88(11)	C(17)-C(20)-H(20C)	109.5
N(2)-C(1)-Zr(1)	123.30(11)	H(20A)-C(20)-H(20C)	109.5
C(1)-N(1)-C(2)	110.60(14)	H(20B)-C(20)-H(20C)	109.5
C(1)-N(1)-C(11)	125.07(14)	C(13)-C(14)-C(15)	123.69(16)
C(2)-N(1)-C(11)	124.20(13)	C(13)-C(14)-H(14)	118.2
C(16)-C(11)-C(12)	121.39(15)	C(15)-C(14)-H(14)	118.2
C(16)-C(11)-N(1)	117.81(14)	C(16)-C(15)-C(14)	116.97(15)
C(12)-C(11)-N(1)	120.78(14)	C(16)-C(15)-C(21)	118.97(15)

C(14)-C(15)-C(21)	124.06(15)	C(5)-C(4)-H(4)	119.2
C(24)-C(21)-C(23)	107.69(15)	C(6)-C(5)-C(4)	121.47(16)
C(24)-C(21)-C(15)	112.32(14)	C(6)-C(5)-H(5)	119.3
C(23)-C(21)-C(15)	109.42(14)	C(4)-C(5)-H(5)	119.3
C(24)-C(21)-C(22)	108.52(16)	C(5)-C(6)-C(7)	117.06(16)
C(23)-C(21)-C(22)	109.48(16)	C(5)-C(6)-H(6)	121.5
C(15)-C(21)-C(22)	109.36(14)	C(7)-C(6)-H(6)	121.5
C(21)-C(22)-H(22A)	109.5	C(2)-C(7)-C(6)	121.40(15)
C(21)-C(22)-H(22B)	109.5	C(2)-C(7)-N(2)	106.08(14)
H(22A)-C(22)-H(22B)	109.5	C(6)-C(7)-N(2)	132.24(15)
C(21)-C(22)-H(22C)	109.5	C(1)-N(2)-C(7)	110.82(14)
H(22A)-C(22)-H(22C)	109.5	C(1)-N(2)-C(31)	124.33(13)
H(22B)-C(22)-H(22C)	109.5	C(7)-N(2)-C(31)	124.46(14)
C(21)-C(23)-H(23A)	109.5	C(36)-C(31)-C(32)	121.50(15)
C(21)-C(23)-H(23B)	109.5	C(36)-C(31)-N(2)	117.60(14)
H(23A)-C(23)-H(23B)	109.5	C(32)-C(31)-N(2)	120.68(14)
C(21)-C(23)-H(23C)	109.5	O(2)-C(32)-C(31)	119.39(15)
H(23A)-C(23)-H(23C)	109.5	O(2)-C(32)-C(33)	122.11(14)
H(23B)-C(23)-H(23C)	109.5	C(31)-C(32)-C(33)	118.43(15)
C(21)-C(24)-H(24A)	109.5	C(32)-O(2)-Zr(1)	141.69(11)
C(21)-C(24)-H(24B)	109.5	C(34)-C(33)-C(32)	117.95(15)
H(24A)-C(24)-H(24B)	109.5	C(34)-C(33)-C(37)	120.97(15)
C(21)-C(24)-H(24C)	109.5	C(32)-C(33)-C(37)	121.06(15)
H(24A)-C(24)-H(24C)	109.5	C(33)-C(37)-C(39)	110.05(14)
H(24B)-C(24)-H(24C)	109.5	C(33)-C(37)-C(38)	112.14(15)
C(15)-C(16)-C(11)	121.15(15)	C(39)-C(37)-C(38)	107.13(15)
C(15)-C(16)-H(16)	119.4	C(33)-C(37)-C(40)	109.38(14)
C(11)-C(16)-H(16)	119.4	C(39)-C(37)-C(40)	110.68(15)
C(3)-C(2)-C(7)	121.33(15)	C(38)-C(37)-C(40)	107.43(15)
C(3)-C(2)-N(1)	132.12(15)	C(37)-C(38)-H(38A)	109.5
C(7)-C(2)-N(1)	106.20(14)	C(37)-C(38)-H(38B)	109.5
C(4)-C(3)-C(2)	117.08(16)	H(38A)-C(38)-H(38B)	109.5
C(4)-C(3)-H(3)	121.5	C(37)-C(38)-H(38C)	109.5
C(2)-C(3)-H(3)	121.5	H(38A)-C(38)-H(38C)	109.5
C(3)-C(4)-C(5)	121.56(16)	H(38B)-C(38)-H(38C)	109.5
C(3)-C(4)-H(4)	119.2	C(37)-C(39)-H(39A)	109.5

C(37)-C(39)-H(39B)	109.5	C(41)-C(44)-H(44B)	109.5
H(39A)-C(39)-H(39B)	109.5	H(44A)-C(44)-H(44B)	109.5
C(37)-C(39)-H(39C)	109.5	C(41)-C(44)-H(44C)	109.5
H(39A)-C(39)-H(39C)	109.5	H(44A)-C(44)-H(44C)	109.5
H(39B)-C(39)-H(39C)	109.5	H(44B)-C(44)-H(44C)	109.5
C(37)-C(40)-H(40A)	109.5	C(35)-C(36)-C(31)	120.79(15)
C(37)-C(40)-H(40B)	109.5	C(35)-C(36)-H(36)	119.6
H(40A)-C(40)-H(40B)	109.5	C(31)-C(36)-H(36)	119.6
C(37)-C(40)-H(40C)	109.5	C(52)-C(51)-Zr(1)	88.09(10)
H(40A)-C(40)-H(40C)	109.5	C(52)-C(51)-H(51A)	114.0
H(40B)-C(40)-H(40C)	109.5	Zr(1)-C(51)-H(51A)	114.0
C(33)-C(34)-C(35)	123.85(16)	C(52)-C(51)-H(51B)	114.0
C(33)-C(34)-H(34)	118.1	Zr(1)-C(51)-H(51B)	114.0
C(35)-C(34)-H(34)	118.1	H(51A)-C(51)-H(51B)	111.2
C(36)-C(35)-C(34)	117.27(15)	C(53)-C(52)-C(57)	117.21(19)
C(36)-C(35)-C(41)	122.13(15)	C(53)-C(52)-C(51)	121.42(19)
C(34)-C(35)-C(41)	120.53(15)	C(57)-C(52)-C(51)	121.15(18)
C(35)-C(41)-C(43)	111.98(14)	C(53)-C(52)-Zr(1)	99.39(12)
C(35)-C(41)-C(42)	108.57(14)	C(57)-C(52)-Zr(1)	107.81(12)
C(43)-C(41)-C(42)	109.43(15)	C(51)-C(52)-Zr(1)	58.79(9)
C(35)-C(41)-C(44)	110.28(14)	C(54)-C(53)-C(52)	120.5(2)
C(43)-C(41)-C(44)	107.51(15)	C(54)-C(53)-H(53)	119.8
C(42)-C(41)-C(44)	109.01(15)	C(52)-C(53)-H(53)	119.8
C(41)-C(42)-H(42A)	109.5	C(55)-C(54)-C(53)	120.8(2)
C(41)-C(42)-H(42B)	109.5	C(55)-C(54)-H(54)	119.6
H(42A)-C(42)-H(42B)	109.5	C(53)-C(54)-H(54)	119.6
C(41)-C(42)-H(42C)	109.5	C(56)-C(55)-C(54)	119.4(2)
H(42A)-C(42)-H(42C)	109.5	C(56)-C(55)-H(55)	120.3
H(42B)-C(42)-H(42C)	109.5	C(54)-C(55)-H(55)	120.3
C(41)-C(43)-H(43A)	109.5	C(55)-C(56)-C(57)	120.5(2)
C(41)-C(43)-H(43B)	109.5	C(55)-C(56)-H(56)	119.7
H(43A)-C(43)-H(43B)	109.5	C(57)-C(56)-H(56)	119.7
C(41)-C(43)-H(43C)	109.5	C(56)-C(57)-C(52)	121.4(2)
H(43A)-C(43)-H(43C)	109.5	C(56)-C(57)-H(57)	119.3
H(43B)-C(43)-H(43C)	109.5	C(52)-C(57)-H(57)	119.3
C(41)-C(44)-H(44A)	109.5	C(101)-B(1)-C(91)	113.86(15)

C(101)-B(1)-C(71)	102.34(14)	F(9)-C(85)-C(86)	120.57(17)
C(91)-B(1)-C(71)	113.45(14)	C(84)-C(85)-C(86)	119.83(17)
C(101)-B(1)-C(81)	112.33(14)	F(10)-C(86)-C(85)	114.30(15)
C(91)-B(1)-C(81)	100.81(13)	F(10)-C(86)-C(81)	121.39(15)
C(71)-B(1)-C(81)	114.58(15)	C(85)-C(86)-C(81)	124.31(17)
C(76)-C(71)-C(72)	113.22(17)	C(92)-C(91)-C(96)	113.47(16)
C(76)-C(71)-B(1)	127.86(16)	C(92)-C(91)-B(1)	126.44(16)
C(72)-C(71)-B(1)	118.48(16)	C(96)-C(91)-B(1)	119.46(15)
F(1)-C(72)-C(73)	116.06(17)	F(11)-C(92)-C(93)	114.97(16)
F(1)-C(72)-C(71)	119.69(16)	F(11)-C(92)-C(91)	121.18(15)
C(73)-C(72)-C(71)	124.25(19)	C(93)-C(92)-C(91)	123.85(17)
F(2)-C(73)-C(74)	119.46(18)	F(12)-C(93)-C(94)	119.59(16)
F(2)-C(73)-C(72)	120.7(2)	F(12)-C(93)-C(92)	120.44(17)
C(74)-C(73)-C(72)	119.85(19)	C(94)-C(93)-C(92)	119.96(18)
F(3)-C(74)-C(73)	120.7(2)	F(13)-C(94)-C(95)	120.73(18)
F(3)-C(74)-C(75)	120.6(2)	F(13)-C(94)-C(93)	120.42(18)
C(73)-C(74)-C(75)	118.76(18)	C(95)-C(94)-C(93)	118.85(17)
F(4)-C(75)-C(74)	120.31(19)	F(14)-C(95)-C(94)	119.73(17)
F(4)-C(75)-C(76)	120.2(2)	F(14)-C(95)-C(96)	120.85(18)
C(74)-C(75)-C(76)	119.5(2)	C(94)-C(95)-C(96)	119.42(18)
F(5)-C(76)-C(71)	121.00(16)	F(15)-C(96)-C(95)	116.25(17)
F(5)-C(76)-C(75)	114.55(18)	F(15)-C(96)-C(91)	119.29(16)
C(71)-C(76)-C(75)	124.46(19)	C(95)-C(96)-C(91)	124.45(18)
C(86)-C(81)-C(82)	112.78(16)	C(102)-C(101)-C(106)	113.04(17)
C(86)-C(81)-B(1)	127.66(16)	C(102)-C(101)-B(1)	127.83(16)
C(82)-C(81)-B(1)	119.16(15)	C(106)-C(101)-B(1)	118.99(16)
F(6)-C(82)-C(83)	115.72(16)	F(16)-C(102)-C(103)	115.15(18)
F(6)-C(82)-C(81)	119.42(16)	F(16)-C(102)-C(101)	120.60(16)
C(83)-C(82)-C(81)	124.85(17)	C(103)-C(102)-C(101)	124.25(19)
F(7)-C(83)-C(84)	119.76(17)	F(17)-C(103)-C(104)	119.74(18)
F(7)-C(83)-C(82)	120.83(17)	F(17)-C(103)-C(102)	120.59(19)
C(84)-C(83)-C(82)	119.41(17)	C(104)-C(103)-C(102)	119.7(2)
F(8)-C(84)-C(85)	120.50(17)	F(18)-C(104)-C(105)	120.4(2)
F(8)-C(84)-C(83)	120.69(17)	F(18)-C(104)-C(103)	120.6(2)
C(85)-C(84)-C(83)	118.79(17)	C(105)-C(104)-C(103)	119.06(18)
F(9)-C(85)-C(84)	119.58(16)	F(19)-C(105)-C(104)	120.26(18)

F(19)-C(105)-C(106)	120.7(2)
C(104)-C(105)-C(106)	119.02(19)
F(20)-C(106)-C(105)	116.02(17)
F(20)-C(106)-C(101)	119.12(17)
C(105)-C(106)-C(101)	124.84(19)
C(3S)-O(1S)-C(1S)	112.92(16)
O(1S)-C(1S)-C(2S)	109.5(2)
O(1S)-C(1S)-H(1S1)	109.8
C(2S)-C(1S)-H(1S1)	109.8
O(1S)-C(1S)-H(1S2)	109.8
C(2S)-C(1S)-H(1S2)	109.8
H(1S1)-C(1S)-H(1S2)	108.2
C(1S)-C(2S)-H(2S1)	109.5
C(1S)-C(2S)-H(2S2)	109.5
H(2S1)-C(2S)-H(2S2)	109.5
C(1S)-C(2S)-H(2S3)	109.5
H(2S1)-C(2S)-H(2S3)	109.5
H(2S2)-C(2S)-H(2S3)	109.5
O(1S)-C(3S)-C(4S)	108.57(18)
O(1S)-C(3S)-H(3S1)	110.0
C(4S)-C(3S)-H(3S1)	110.0
O(1S)-C(3S)-H(3S2)	110.0
C(4S)-C(3S)-H(3S2)	110.0
H(3S1)-C(3S)-H(3S2)	108.4
C(3S)-C(4S)-H(4S1)	109.5
C(3S)-C(4S)-H(4S2)	109.5
H(4S1)-C(4S)-H(4S2)	109.5
C(3S)-C(4S)-H(4S3)	109.5
H(4S1)-C(4S)-H(4S3)	109.5
H(4S2)-C(4S)-H(4S3)	109.5

[i] Sheldrick, G. M. *Acta Cryst.* **1990**, A46, 467-473.

[ii] Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112-122.

[iii] Müller, P. *Crystallography Reviews* **2009**, *15*, 57-83.